TEXTILE RESEARCH JOURNAL

Publication of

TEXTILE RESEARCH INSTITUTE

FEBRUARY 1960 NUMBER 2

TEXTILE RESEARCH JOURNAL

Volume 30 *February 1960* Number 2

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the Publications Department, P.O. Box 625, Princeton, N. J.

Second-class postage paid at Lancaster, Pa.

Subscription rates: $25.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $2.50 each.

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FEBRUARY 1960
VOL. 30 NO. 2

TEXTILE RESEARCH JOURNAL

Cotton Quality Study

IV: Resistance to Weathering

John W. Howard[1] and Frank A. McCord[2]

National Cotton Council of America, Washington, D. C.

Introduction

Weathering is an inclusive term describing the aggregate effect of environmental factors of sunlight, microorganisms, industrial fumes, rain, and wind. Few materials escape the destructive action of the weather. Over prolonged periods, wood, steel, and even stone are attacked by the elements. When textiles are used outdoors, deterioration in both strength and appearance takes place until ultimately replacement becomes necessary.

As a natural fiber, cotton is subjected at a very early stage to the deteriorating effects of weather. From the moment the boll opens in the field until the cotton is harvested and taken to the gin, the fiber is exposed to damage from sunlight, microorganisms, and other atmospheric conditions which greatly influence its market value. Overexposure in the field affects the fiber's luster, color, and strength. Microbial damage may also take place during storage at various stages in manufacturing. During service few cotton products completely avoid exposure to the degradative action of weather, and for many uses weathering is a major consideration.

Cotton long has been and still is the principal fiber used in outdoor fabrics. Because of the multitude of end-uses, cotton fabrics are subjected to a wider range of weathering conditions than any other textile material. Cotton textiles are employed in such varied civilian and military outdoor products as tents, tarpaulins, awnings, and truck covers, to name only a few. Even for fabrics used only indoors, one or more of the factors of weathering can affect their appearance and durability. For instance, draperies in windows are acted on by the sun's rays, and towels or clothing are frequently damaged by microbial action if allowed to remain wet for any length of time. Resistance to weathering is important in markets consuming the equivalent of over two and one half million bales of cotton annually.

Weatherproofing finishes for cotton offer the chemical industry potentially large markets if more efficient, economical treatments can be developed. Based on the present annual consumption of over 600 million pounds of cotton fiber (equivalent to about 550 million pounds of yarn or fabric) used in products exposed to weather, a treatment using as little as 5% of the weight of the cotton would consume a minimum of 27 million pounds of chemicals yearly.

This report points out where and to what extent the need and opportunity exists for improving cotton's weather resistance. Its purpose is to stimulate

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research by reviewing and condensing technical knowledge in the field and by suggesting new approaches for further study.

Part I: Market Analysis

An evaluation of weathering as an influence on cotton usage must recognize these important aspects of the subject:

Effect on Consumer Product Usefulness or Service Life—Is degradation caused by weathering severe enough to be recognized by consumers? If so, do consumers associate the damage with weathering? Is the dissatisfaction strong enough to cause consumers to switch to competing materials or to stop using the product?

Competition for End Use Markets—Is the lack of resistance to weathering important enough to enable competing materials to displace cotton in traditional outlets?

Potential for Process to Improve Weathering Qualities—Is the potential for an effective weathering treatment for cotton large enough to attract the resources required to develop and put such a process into commercial application?

These questions can be answered only through an examination of the end use textile outlets in which weathering is a factor.

End Use Evaluation

Cotton textile products subjected to weathering may be grouped into four classifications depending upon the extent of the degradative influence to which they are exposed.

Group I: *Products subjected to frequent or continuous outdoor exposure*—Awnings, tents, and fishing supplies are prime examples of uses in which cotton textile products are subject to frequent or continuous outside exposure in regular or customary use practices.

Group II: *Products subjected to frequent and lengthy exposures to sunlight, wind, humidity, etc., but not to outside exposure*—Automobile upholstery, window shades, and window curtains are illustrative of uses which generally are not subjected to outside exposure but which are frequently or continuously exposed to sunlight, wind, and humid air.

Group III: *Products subjected to microbiological attack, but not to outside exposure*—Mattress felts, towels, and shower curtains represent uses in which cotton products are subjected to deterioration from mildew. However, most consumers do not associate such damage with weathering. Similarly, service apparel worn in industrial plants and similar locations may deteriorate rapidly as a result of airborne acids or other chemical agents. Again, most consumers do not associate such deterioration with weathering.

Group IV: *Products infrequently subjected to outdoor exposure and to exposures to sunlight, wind, and other elements of weathering*—Virtually all apparel and household products regularly worn or used outside, or which are washed and dried in sunlight and air, could be included in this group. While such items are subjected to the influence of weathering during brief exposures, weathering usually is not considered to be a principal cause of degradation, except perhaps in some work apparel worn by laborers during summer months. Although weathering may be a factor in the service life of these products, it is almost impossible to segregate and measure the volume of materials consumed under such conditions or to determine the influence of weathering on service life. Therefore, uses falling into this group are not considered further in this evaluation. The fact must be recognized, however, that weathering is a consideration and that improvements in resistance to weathering would strengthen cotton's position in this classification.

Tabulations in the volume of cotton and other textile materials consumed in applications subjected to the influences of weathering are detailed in Tables I, II, and III and summarized in Table IV.

Market Potential

The statistics indicate that:

1. Weathering is important in textile outlets consuming more than 1,363,573,000 lb. of all fibers annually, the equivalent of more than 2,700,000 bales of cotton;

2. Weathering is important in textile outlets consuming more than 614,496,000 lb. of cotton yearly, or the equivalent of more than 1,200,000 bales of cotton;

3. Degradation resulting from:

a. outside exposure is important in uses consuming 154,650,000 lb. of cotton materials annually, or about 300,000 bales;

b. exposure to sunlight, wind, etc., not under conditions of outside exposure, is important in uses accounting for 189,354,000 lb. of cotton materials annually, or about 375,000 bales;

TABLE I. Estimated Consumption of Materials in Uses Subjected to Outdoor Exposure[1]

	1,000 Lb. fiber consumption[2]		Portion of market affected[3]		
	Total size of market, all materials	Total cotton consumption	Percent	1,000 Lb. fiber consumption[2]	
				All materials	Cotton
Automobile tops, convertible	4,534	4,395	100	4,534	4,395
Awnings	25,272	24,005	100	25,272	24,005
Bags, mail	4,505	4,505	100	4,505	4,505
Belts, conveyor and elevator	25,260	20,460	35	8,841	7,165
Cordage and twine	342,330	43,205	25	85,583	10,801
Fishing supplies					
Fish lines	1,494	600	100	1,494	600
Netting	3,940	2,560	100	3,940	2,560
Seine twine	5,683	4,265	100	5,683	4,265
Flags	2,738	2,190	80	2,190	1,752
Friction tape	5,218	4,175	5	261	209
Hose, fire	6,517	4,950	75	4,888	3,712
Industrial thread	78,454	72,875	5	3,923	3,644
Insulation, electrical	147,088	33,830	20	29,418	6,766
Irrigation equipment and supplies[4]	25,000	1,000	100	25,000	1,000
Pick sacks, cotton	5,690	5,690	100	5,690	5,690
Shoes					
Laces	2,321	2,180	60	1,393	1,308
Uppers	117,410	15,265	60	70,446	9,159
Sporting equipment	2,994	2,305	80	2,395	1,844
Tarpaulins	35,038	29,435	100	35,038	29,435
Tents	25,365	25,365	100	25,365	25,365
Tobacco cloths	5,730	5,730	100	5,730	5,730
Umbrellas					
Beach, garden, tractor	786	705	100	786	705
Hand	906	35	100	906	35
Total	912,305	309,725	—	353,281	154,650

[1] Applications in which textile products are subjected to frequent or continuous outdoor exposure.
[2] Based on data in "Cotton Counts Its Customers," National Cotton Council of America, 1959, unless otherwise noted.
[3] Estimated percentage of total usage subjected to such deterioration.
[4] Industry estimate.

TABLE II. Estimated Consumption of Materials in Uses Subjected to Frequent and Lengthy Exposure to Sunlight, Wind, Etc.[1]

	1,000 Lb. fiber consumption[2]		Portion of market affected[3]		
	Total size of market, all materials	Total cotton consumption	Percent	1,000 Lb. fiber consumption[2]	
				All materials	Cotton
Automobile					
Seat covers	69,938	11,855	100	69,938	11,855
Upholstery and linings	97,667	38,590	100	97,667	38,590
Curtains	57,535	16,535	100	57,535	16,535
Draperies[4]	242,391	147,859	75	181,793	110,894
Venetian blind tapes	3,840	2,420	100	3,840	2,420
Window shades	17,427	9,060	100	17,427	9,060
Total	488,798	226,319	—	428,200	189,354

[1] Not due to outside exposure.
[2] Based on data in "Cotton Counts Its Customers," National Cotton Council of America, 1959, except draperies.
[3] Estimated percentage of total usage subjected to such deterioration.
[4] Estimated on basis of data developed in study of usage of fabrics in draperies and upholstery.

TABLE III. Estimated Consumption of Materials in Uses Subjected to Microbiological Attack, Not Due to Outside Exposure[1]

	1,000 Lb. fiber consumption[2]		Portion of market affected[3]		
	Total size of market, all materials	Total cotton consumption	Percent	1,000 Lb. fiber consumption[2] All materials	Cotton
Diapers	36,575	36,575	100	36,575	36,575
Filter cloths	6,608	4,825	25	1,652	1,206
Laundry wash nets	7,729	2,320	100	7,729	2,320
Luggage linings	9,771	1,955	25	2,443	489
Mattress and box spring felts	288,679	2,885	50	144,340	1,443
Rugs and carpets	562,359	111,145	25	140,590	27,786
Shoe linings	50,143	32,095	75	37,607	24,071
Shower curtains	19,168	960	100	19,168	960
Table cloths and napkins	24,269	19,590	50	12,135	9,795
Towels	195,757	185,970	75	146,818	139,477
Washable service apparel	66,071	52,740	50	33,035	26,370
Total	1,267,129	451,060	—	582,092	270,492

[1] "Weathering" usually is not recognized as the cause of degradation in these outlets.
[2] Based on data in "Cotton Counts Its Customers," National Cotton Council of America, 1959.
[3] Estimated percentage of total usage subjected to such deterioration.

TABLE IV. Market Potential for Treatment to Improve Weathering Qualities of Textiles

Description	1,000 Lb. fiber consumption All materials	Cotton
Potential in uses subjected to outside exposure	353,281	154,650
Potential in uses subjected to sunlight, wind, etc.	428,200	189,354
Potential in uses subjected to microbiological attack, not due to outside exposure	582,092	270,370
	1,363,573	614,496

c. microbiological attack not caused by outside exposure is important in uses accounting for 270,492,000 lb. of cotton materials annually, or about 540,000 bales.

Studies of consumer buying practices, fiber preferences, and desired quality improvements show conclusively that degradation from weathering in many outlets is severe enough to be recognized by consumers, and that consumers do associate the degradation with some of the elements of weathering, particularly in the uses covered in Tables I and II.[3] In most applications, a serious impairment of appearance resulting from stains or loss of color may cause consumer dissatisfaction before there is a noticeable loss of strength or a deterioration in other performance characteristics.

Statistical tabulations of the consumption of cotton and other materials by major end uses suggest that unsatisfactory weathering qualities of cotton materials have been a factor in the gains of competing materials in some applications such as awnings and tarpaulins.[4] In these, and in many other outlets, the loss potential for cotton is quite large unless improvements are made in its weathering qualities and if satisfactory substitute materials can be found or developed at competitive prices on a use-performance basis.

As shown in Table IV, over 1.3 billion pounds of all textiles and over 0.6 billion pounds of cotton products alone go into uses which are subjected to weathering. It would appear that this volume should be large enough to attract the research and development funds needed to develop protective treatments. The potential for a specific treatment, however, may be quite different from the gross potential, depending on the:

a. extent to which the treatment is effective against different types of weathering;
b. cost;
c. degree to which service life is extended;
d. effects of the treatment on other qualities.

[3] See list of consumer and industry studies following Table V.

[4] "Cotton Counts Its Customers," National Cotton Council of America, 1959.

TABLE V. Competitive Factors in End Uses in which Weathering is Important*

End use	Principal quality requirements	Principal competitors	Basis of competition with cotton	Price relationships
	Group 1: Uses subjected to frequent or continuous outdoor exposure			
Automobile tops, convertible[1]	Dimensional stability, fast dyes, quick drying; resistance to abrasion, fraying, mildew and rot, soiling, and staining; water repellency, tensile strength, adhesive qualities	Rayon	Appearance	Cotton lower in cost than rayon
Awnings[2]	Fast dyes, water repellency, dimensional stability, quick drying; resistance to mildew and rot, fraying, fire, staining	Aluminum	Long service life and low maintenance cost; fixed installation	Initial cost of aluminum many times cost of cloth awnings
Bags, mail	Resistance to mildew and rot, tensile strength	Nylon	Cost and service life	Cotton cheaper than nylon
Belts, conveyor and elevator[3]	Tensile strength, low extensibility, adhesion with rubber, low bulk, resistance to abrasion, flexing, fraying, mildew and rot, heat	Rayon, nylon, glass fiber	High strength	Rayon holds price advantage in high strength belts; nylon and glass more expensive
Cordage and twine[4]	Dimensional stability, high tensile strength, low bulk, quick drying; resistance to abrasion, mildew and rot, soiling	Hard fibers, some nylon and rayon, paper tapes	Price, low bulk, and high strength	Paper tapes and fibers, except nylon, cheaper than cotton
Fishing supplies[4]	Dimensional stability, quick drying, resistance to mildew and rot, abrasion, chemicals, fraying, soiling, staining; high tensile strength, lightweight, low moisture absorption	Nylon, linen silk	High strength and durability	Linen and nylon lower priced than cotton on strength basis
Flags[5]	Dimensional stability, fast dyes, quick drying, high tensile strength, resistance to abrasion, fraying, mildew and rot, staining, snagging, soiling	Wool, nylon, rayon	Wool and nylon, appearance and durability; rayon, price	Cotton lower in price than wool or nylon and about equal to rayon
Friction tape	Adhesive qualities, insulating properties, low bulk; resistance to abrasion, chemicals, heat, linting	Plastic	Price and low bulk	Much cheaper than cotton
Hose, fire[6]	Tensile strength, low bulk, lightweight; resistance to abrasion, heat, mildew and rot, oil, grease, chemicals	Dacron, linen	Dacron, lightweight and durable; linen, price	Dacron much higher than cotton; linen about equal to cotton

* Source: Basic data drawn from "Some Factors Influencing Cotton's Competitive Position in Domestic Markets," an unpublished manuscript of the National Cotton Council of America, November 1956, supplemented by information from published studies and reports as indicated.

[1] "Automobile Manufacturers Discuss Fabrics and Fibers for Passenger Cars," October 1951, United States Department of Agriculture, Bureau of Agricultural Economics, Agricultural Information Bulletin No. 45; "Fabrics and Fibers for Passenger Cars," April 1957, United States Department of Agriculture, Marketing Research Report No. 152.

[2] "Survey of Canvas Awning Fabricators," United States Department of Agriculture, Bureau of Agricultural Economics, Marketing Research Report No. 1, April 1952; "Cotton Duck, Industry, Products, Uses," National Cotton Council of America, January 1956.

[3] "Cotton in the Belting Industry," National Cotton Council of America, March 1952.

[4] "Fibers, Opinions, and Practices Among Manufacturers of Cordage and Twine," United States Department of Agriculture, Bureau of Agricultural Economics, Marketing Research Report No. 51, June 1953; "Cotton in Industrial Tapes," National Cotton Council of America, May 1957.

[5] "The American Flag and American Cotton," National Cotton Council of America, June 1950.

[6] "Cotton in Industrial Hose," National Cotton Council of America, April 1952.

TABLE V (Continued)

End use	Principal quality requirements	Principal competitors	Basis of competition with cotton	Price relationships
Industrial thread[7]	Dimensional stability, fast dyes, luster, high tensile strength, resistance to abrasion, chemicals, fraying, mildew and rot, soiling	Nylon, Orlon[17]	High strength, low bulk, and durability	Not important competitive factor at this time
Insulation, electrical[8]	Elasticity, insulating properties, lightweight, low bulk, quick drying; resistance to abrasion, chemicals, heat, linting; tensile strength, and water repellency	Plastic, Fiberglas,[18] paper, rayon	Plastic, price and performance; Fiberglas, heat resistance; paper, price; rayon, price	Plastic, paper and rayon lower than cotton; Fiberglas higher than cotton
Irrigation equipment and supplies	Waterproof, resistance to mildew and rot, abrasion, fraying, chemicals; lightweight, low bulk	Plastic, metal	Longer service life	Cotton much lower in initial cost
Pick sacks, cotton	Resistance to abrasion, mildew and rot, chemicals, snagging; tensile strength	None	—	—
Shoelaces[9]	Tensile strength, fast dyes, luster; resistance to abrasion, fraying, mildew and rot, slipping	Nylon	Durability and appearance	Nylon higher priced than cotton
Shoe Uppers[9]	Adhesive qualities, dimensional stability, fast dyes, nonirritating, water repellency, quick drying, tensile strength; resistance to abrasion, flexing, mildew, odors, scuffing, snagging, soiling, staining	Leather, plastic	Durability and appearance	Leather much higher priced than cotton; plastic lower
Sporting equipment	Dimensional stability, fast dyes, lightweight, low bulk, luster, quick drying, water repellency, tensile strength; resistance to abrasion, fraying, mildew and rot, scuffing, soiling, staining	Leather and plastic	Durability and prestige for leather, price and durability for plastic	Leather much higher priced than cotton; plastic lower priced than leather but higher than cotton
Tarpaulins[2]	Dimensional stability, fast dyes, lightweight, low bulk, quick drying, water repellency, tensile strength; resistance to abrasion, chemicals, fire, fraying, mildew and rot, snagging, staining, wind	Nylon, plastic, paper	Nylon, lightweight and durability; plastic, price; paper, price and convenience	Nylon higher priced than cotton; plastic and paper lower than cotton
Tents[2]	Dimensional stability, fast dyes, lightweight, low bulk, quick drying, water repellency, tensile strength; resistance to abrasion, chemicals, fire, fraying, mildew and rot, snagging, soiling, staining, wind	Very small quantities of nylon	Lightweight	Higher priced than cotton
Tobacco cloth	Lightweight; resistance to fire, mildew and rot, chemicals	Plastic	Service life	Higher priced than cotton
Umbrellas	Water repellency, dimensional stability, fast dyes, lightweight, luster, quick drying; resistance to fire, fraying, mildew and rot, snagging, soiling, staining	Rayon and plastic	Rayon, appearance and price; plastic, price	Rayon and plastic lower priced than cotton

[7] "The Demand for Extra-Long Staple Cotton," National Cotton Council of America, December 1953.
[8] "Fibers Used in Insulated Wire and Cable," United States Department of Agriculture, April 1955.
[9] "Cotton in the Shoe Industry," National Cotton Council of America, September 1948.

TABLE V (Continued)

End use	Principal quality requirements	Principal competitors	Basis of competition with cotton	Price relationships
Group II: Uses subjected to frequent and lengthy exposures to sunlight and wind but not to outdoor exposure				
Automobile seat covers[10]	Absorbency, adhesive qualities, coolness, dimensional stability, fast dyes, luster, quick drying, slipperiness, water repellency, tensile strength; resistance to abrasion, chemicals, fire, fraying, scuffing, soiling, static electricity	Paper, plastic, nylon, rayon	Paper, price; plastic, durability; nylon, durability; rayon, appearance and price	Plastic and nylon higher in price than cotton; most rayon higher than cotton; paper cheaper than cotton
Upholstery and linings[1]	Absorbency, coolness, dimensional stability, elasticity, fast dyes, luster, quick drying, water repellency, warmth, tensile strength, soft colors, slipperiness, resistance to abrasion, chemicals, fire, fraying, mildew, odors, pilling, scuffing, snagging, soiling, static electricity, staining	Wool, nylon, plastic, rayon	Wool, appearance and prestige; nylon, appearance and durability; plastic, price and soil resistance; rayon, appearance and price	Wool and nylon much higher than cotton; plastic slightly higher than cotton; rayon about equal to cotton or slightly lower
Curtains, window	Dimensional stability, fast dyes, luster, crispness, quick drying, soft colors, sheerness; resistance to fire, fraying, snagging, soiling, staining	Orlon, nylon, Fiberglas, dacron	Ease of maintenance	All competitors higher in price than cotton
Draperies[11]	Crease resistance, dimensional stability, drape, fast dyes, luster, vivid prints, resistance to abrasion, fire, fraying, odors, snagging, soiling	Rayon, nylon, Fiberglas	Rayon, price and luster; nylon, luster and durability; Fiberglas, ease of care, resistance to fire	Rayon lower in cost than cotton; Fiberglas higher than cotton; nylon higher than cotton
Venetian blind tape	Dimensional stability, fast dyes, low bulk, luster, quick drying, tensile strength; resistance to abrasion, fraying, soiling, staining	Plastic, rayon	Plastic, resistance to soil and cleanability; rayon, appearance	Plastic higher priced than cotton; rayon slightly lower in cost
Window shades	Dimensional stability, fast dyes, low bulk, water repellency, soft colors; resistance to abrasion, fire, heat, snagging, soiling	Paper	Price	Paper much cheaper than cotton
Group III: Uses subjected to microbiological attack, not due to outside exposure				
Diapers	Absorbency, nonirritating, no ironing, quick drying, dimensional stability; resistance to abrasion, chemicals, mildew	Paper	Price and convenience	Initial cost lower than cotton; cotton cost lower on re-use basis
Filter cloths[12]	Tensile strength, absorbency, dimensional stability, low bulk, quick drying, resistance to abrasion, chemicals, heat, linting, mildew, staining	Metal, wool, nylon, Dynel, paper, rayon	Strength, durability, price	Cotton lower priced than all competitors except paper and rayon
Laundry wash nets[13]	Lightweight, low bulk, quick drying; resistance to abrasion, chemicals, mildew, snagging	Nylon	Lightweight, low bulk, quick drying, mildew resistance	Initial cost of nylon higher than cotton

[10] "The Market for Automobile Seat Covers," Chicopee Mills, March 1955.
[11] "Cotton Fabrics in Upholstery, Drapes, and Slip Covers," National Cotton Council of America, April 1953.
[12] "Cotton in Filter Fabrics," National Cotton Council of America, January 1957.
[13] "Cotton in the Laundry Industry," National Cotton Council of America, September 1949.

TABLE V (Continued)

End use	Principal quality requirements	Principal competitors	Basis of competition with cotton	Price relationships
Luggage linings[14]	Fast dyes, lightweight, low bulk, luster; resistance to abrasion, mildew, snagging, soiling, staining	Rayon and acetate	Appearance	About same as cotton
Mattress and box spring felts	Resiliency, absorbency; resistance to mildew, odors, soiling, staining	Foam rubber, plastic foam	Resiliency	Cotton cheaper than rubber and plastic foam
Rugs and carpets[15]	Resiliency, luster, fast dyes, dimensional stability, soft colors; resistance to abrasion, odors, mildew, soiling, staining	Nylon, wool, rayon	Appearance, durability, prestige	Cotton cheaper than all competitors except rayon; rayon and cotton about competitive in price
Shoe linings[9]	Quick drying, nonirritating, water repellency; resistance to abrasion, mildew, rot, odors, chemicals, soiling	Leather, rayon	Durability, prestige, appearance, price	Leather much higher than cotton; rayon about competitive with cotton
Shower curtains	Quick drying, water repellency, luster, vivid prints, fast dyes; resistance to mildew, fraying, soiling, staining	Plastic, nylon, glass	Price, appearance, ease of maintenance	Cotton cheaper than nylon and glass, but more costly than plastic
Table cloths and napkins[16]	Absorbency, dimensional stability, fast dyes, luster, no ironing, soft colors, vivid prints; resistance to mildew, linting, soiling, staining	Plastic, rayon, linen	Price, appearance, prestige	Cotton cheaper than linen, about competitive with rayon, and more costly than plastic
Towels[16]	Absorbency, fast dyes, nonirritating, quick drying, soft colors; resistance to abrasion, linting, mildew, staining	Paper, linen	Convenience, prestige	Paper lower than cotton in initial cost. Linen more expensive than cotton
Washable service apparel[16]	Dimensional stability, luster, ease of care, nonirritating, quick drying; resistance to chemicals, mildew, odors, soiling, staining	Dacron, nylon	Ease of care	Cotton lower in initial cost

[14] "Cotton in the Luggage Industry," National Cotton Council of America, May 1950.
[15] "Market Potential for Carpets and Rugs," National Cotton Council of America, February 1956.
[16] "Cotton in the Linen Supply Industry," National Cotton Council of America, December 1949.
[17] Du Pont trademark.
[18] Owens Corning trademark.

The demand for a treatment effective against some elements of weathering, but not against all elements, would be considerably smaller than the demand for a treatment which protected against all types of weathering. For instance, the demand for a treatment which improved cotton's resistance to microorganisms, without any improvement in resistance to sunlight, would be much smaller than the demand for a treatment which provided better protection against both.

Cost is a primary consideration in the demand potential for any finish. If the cost of improving the weathering qualities of textile products substantially reduces favorable price differentials for cotton, gives competing materials a price advantage, or causes consumers to reduce their total purchases, the potential will be less than indicated in Table IV. To illustrate, if costs of treating duck to achieve better resistance to weathering in awnings were high enough to reduce materially or to eliminate the price differential between cloth and metal awnings, the potential market for the finish would be substantially reduced.

Improvements in the service life of cotton products, on the other hand, would justify some price increases in most outlets, without limiting expansion opportunities. For example, if the service life of cotton awnings could be doubled, the cost of awning fabrics might be increased by 50–100% without an adverse effect on the demand for cotton awnings, since fabric cost represents only a small fraction of the total cost of an awning and because a longer service life for cotton awnings would provide opportunities for competitive gains against metal awnings. Metal frames, installation, storage, and repairs represent major cost

factors in the price of cotton awnings. An increased service life would enable total costs to be spread over a longer period of time. Many prospective customers for metal awnings would find cloth awnings more attractive if they had assurance of longer service life.

The effects of specific weathering treatments on other fabric qualities will influence the size of the market potential. Treatments which adversely affect other desirable qualities will find limited markets. Treatments which enhance desirable properties will find a stronger demand than treatments which improve weathering qualities alone. A process which doubled the service life of awning fabrics would have little or no value if the treated fabric would not take and retain desired colors or if it were difficult or impossible to sew the fabrics. If the treatment resulted in brighter, fadeproof colors, the demand potential would be larger than if improvements were limited to weathering.

Competitors, quality requirements, and cost relationships differ widely among the uses in which improvements in weather resistance are desirable. Information about quality requirements, competitors, and price relationships is summarized in Table V. This information, the quantity data in Tables I, II, and III, and a knowledge of the performance characteristics of a particular treatment provide a basis for estimating the rough market potentials for specific treatments which may be developed to improve the weathering qualities of cotton textiles, or of all textiles.

Part II: Technical Section

Structure of Cotton

The following brief discussion on the structure of the cotton fiber is included here only for the information of those readers who may not be familiar with the terminology used in this paper. Comprehensive reviews on this subject are readily available [245, 333].

Typical cotton fibers contain about 94% cellulose and 6% of other ingredients consisting of waxes, pectins, proteins, pigments, and inorganic compounds. Cotton cellulose is composed of anhydroglucose units joined through an ether linkage into long, linear, chainlike molecules held together laterally by hydrogen bonds. The empirical formula may be written as $(C_6H_{10}O_5)_n$, where n represents the number of anhydroglucose units in the molecule. The average value of n in native cotton fibers is 3000 or greater and may be as high as 8,000–10,000. The structural formula for cellobiose, the basic unit of cellulose consisting of two anhydroglucose units linked together, is given in Figure 1. Each anhydroglucose unit contains a primary and two secondary hydroxyl groups which react chemically as alcohols.

Mature cotton fibers, as characterized by x-ray diffraction methods, contain both amorphous (disordered) and crystalline (ordered) regions. For cellulose to give a crystalline x-ray diffraction pattern, the anhydroglucose units must be arranged in a regular and repeated fashion. Various methods of measurement indicate that native cotton cellulose has a degree of crystallinity of from 50 to 94%. The amorphous or less well-ordered regions are more accessible to reagents and are more easily swollen and more reactive than the crystalline areas.

As shown in Figure 2, the cotton fiber is composed of three main parts: the outer primary wall, the secondary wall, and the central canal or lumen. The primary wall or outer cell wall of the fiber contains some crystalline cellulose, but it is composed mostly of amorphous cellulose, pectic materials, and waxes.

The secondary wall makes up the bulk of the cotton fiber and consists of a tree-like, ring-layered structure associated with cycles of rapid and slow growth during the development of the fiber on the plant. Each growth ring is made up of two adjacent layers, one much more compact than the other. Under normal conditions, a complete ring is deposited every 24 hr., and it is believed that the dense layer is produced during the day and the less com-

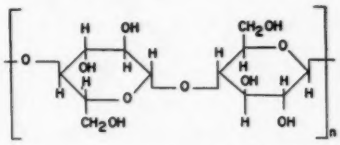

Fig. 1. The formula for cellulose, showing a cellobiose unit.

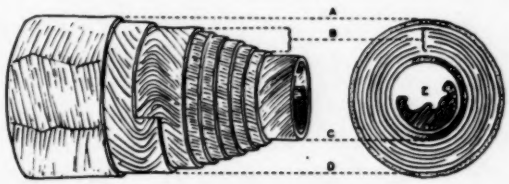

Fig. 2. Diagram illustrating the longitudinal and cross-sectional structure of a cotton fiber. A, primary wall; B, central region; C, inner layer; D, outer layer of secondary thickening; and E, lumen-containing residue of protoplasm.

pact one at night. Innumerable microfibrils are aligned in a spiral fashion along the longitudinal axis of the fiber in each layer. The direction of these spirals reverses from time to time. The microfibrils are aggregates of cellulose molecules and range from 100 to 200 Å in width [326].

The lumen runs the length of the fiber, except near the tip. In mature fibers, it contains the debris from the dead protoplasm. The lumen dimension varies with both the variety and the environmental conditions under which the cotton is grown.

Mechanisms of Weathering

Deterioration of textiles from weathering may be classified as chemical or physical. The chief agencies causing chemical deterioration are sunlight (photochemical or actinic degradation) and mildew or rot (microbial attack). Other chemical factors such as airborne acids and alternate wetting and drying may also contribute, but have less effect. Physical deterioration, on the other hand, occurs as the result of fiber damage due to rubbing, flexing, or repeated tensioning caused by wind, alternate freezing and thawing, and dust abrasion.

The relative importance of these factors varies with location and time of year. For example, in this hemisphere photochemical and microbiological activity are both at a maximum during the months of June, July, and August, and at a considerably lower level during the winter months of January, February, and March [88].

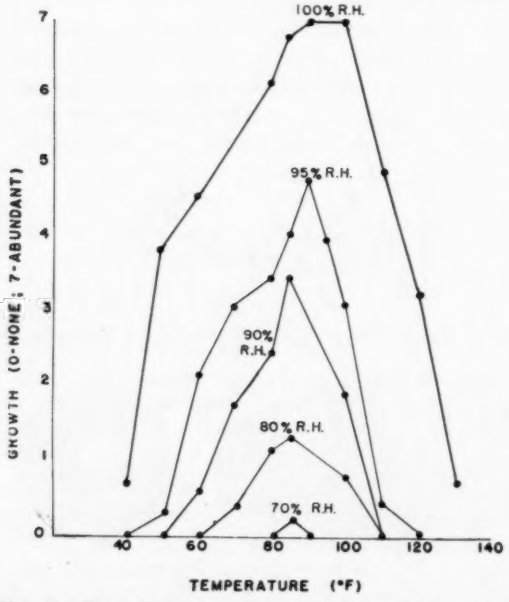

Fig. 3. The effect of various conditions of temperature and relative humidities on the growth of fungi.

In the southern states, both microbial action and sunlight are important sources of attack, since the warm temperatures and humid conditions favor the growth of microorganisms, and the total amount of sun is high. In the North, sunlight is a degradant, but its relative importance is considerably less, leaving mildew or rot as the major cause of deterioration. In the southwestern states, sunlight would be the major cause of deterioration because of the dry, sunny weather.

The relative importance of degradants such as airborne acids and abrasion also depends on geographical location and season. In highly populated industrial areas, degradation of fabrics by acid-forming substances in the atmosphere is of considerable importance. Alternate wetting and drying may be a contributing factor to the degradation of textiles in tropical and semitropical regions. The presence of a significant amount of an abradant in the air would occur only in the desert or similar areas where there are dust storms. Self-abrasion and rubbing of the fabric on its surroundings depend on how the textile is used and the weather conditions.

Mildew and Rot

Microbial attack on cellulosic textiles is of two general types. One is predominantly a surface attack in which the microorganisms feed on the material present on the fiber surface without degrading the underlying cellulose. This action is commonly referred to as "mildew." The other type of attack is usually referred to as "rot" and involves the actual disintegration of the fabric through the action of enzymes secreted by the organism. Mildew affects the comfort and appearance of a fabric, while rot affects the serviceability.

The organisms involved in the mildewing or rotting of cellulosic fabrics are fungi, bacteria, and actinomycetes. All belong to the same major division of the plant kingdom, Thallophyta, and to the subdivision Mycophyta, and occur in nature as (1) cellulolytic or cellulose-decomposing organisms and (2) noncellulolytic or surface-growing organisms. Since fungi and bacteria are the most important organisms involved in the deterioration of cellulose, only these two types will be considered.

On the basis of oxygen requirements microorganisms are separated into three classes [300]. Strict aerobes multiply only in the presence of free oxygen, whereas strict anaerobes develop in the absence of free oxygen. Facultative anaerobes, on the other hand, reproduce nearly as well in either of the two conditions. Fungi are mostly strict aerobes, but occasionally may be facultative anaerobes. Strict anaerobes are found only in bacteria, which also include aerobic and facultatively anaerobic members. Cotton textiles are normally used under conditions involving a plentiful oxygen supply. This favors the predominant development of aerobes, either of the fungal or bacterial variety.

The great majority of bacteria and fungi do not require living hosts for their nourishment but are capable of using nonliving, fairly complex organic substances such as sugars etc. in order to provide the energy for the operation of their life processes. Most organisms possessing the ability to deteriorate cellulose require for their existence a supply of oxygen, carbon, nitrogen, phosphorus, magnesium, sulfur, and trace elements such as iron, manganese, and zinc [300]. Many of these needed elements are present in unpurified cotton cellulose but are largely removed in ordinary purification processes such as scouring and bleaching. Scoured and bleached fabrics are, therefore, somewhat more resistant to microorganisms than greige fabrics [88]. On the other hand, many "finished fabrics" contain materials such as starch, dextrin, and tallow, which are more readily attacked than cellulose itself.

One of the most important requirements for the growth of microorganisms is moisture, or more specifically, the proper combination of temperature and moisture. Figure 3 shows the rate of fungal growth plotted against temperature and relative humidity and illustrates the manner in which germination is dependent on these two factors [174]. Fungi require a relative humidity of around 80% for good growth, while bacteria do not ordinarily multiply at humidities below 70%. Temperature is not as critical as humidity, and some fungi can carry on their life processes at temperatures close to freezing or as high as 180° F.

Another important factor related to humidity is the moisture content of the substrate. Fungi will not grow on cotton containing less than 7.5% moisture [16]. Dessication, however, will not destroy the organism. The spores remain dormant and germinate when conditions again become suitable. Profuse growth will occur on cotton when the moisture content exceeds 10% [316]. Actually, the moisture content of cotton is determined to a significant extent by the relative humidity of the atmosphere. At 80% relative humidity cotton contains approximately 10% moisture when in equilibrium with the atmosphere. At present, it is not clear whether the relative humidity of the surrounding atmosphere or the moisture content of the substrate has the greater effect on spore germination [300].

Variations in the pH of the medium have an effect on the activity of certain microorganisms. An acid medium usually favors the growth of fungi which have been observed to attack cellulose at a pH as low as 2.0 [256]. However, some fungi have been shown to be equally active from pH 3.5 to 8.5 [300]. Bacteria appear to have a much narrower range of tolerance to changes in pH than fungi. A slightly alkaline medium, around pH 7.0 to 8.0, is the most favorable for the growth of the majority of the cellulose-destroying bacteria.

Prolonged exposure to sunlight is fatal to cellulolytic organisms, the effect being dependent on the wavelength of the light [166]. Radiation in the visible range is less lethal than certain wave lengths in the ultraviolet range. This explains why profuse mildew growth is frequently observed on the underside of heavy fabrics while the surface exposed to the sun may be almost free from attack. The density of the fabric and its ability to resist the penetration of ultraviolet rays is, therefore, important in determining the type of degradation against which protection must be provided. Heavy or dense fabrics are deteriorated by both sunlight and microorganisms, while with thin fabrics microbiological attack is relatively less important.

The exact mechanism by which cellulolytic fungi degrade cellulosic fibers is not clearly understood. Opinions differ as to whether the deterioration starts from the outside and proceeds inward, or whether the organisms penetrate the lumen and degrade the fibers from the inside out. Experimental evidence supports the former concept, and from histological studies it appears fairly certain that one of the first effects is the digestion of the cuticular layer of the fiber [228, 251, 300, 316]. Figure 4 is a photomicrograph of a cotton fiber under fungus attack. In this instance, the fungal hyphae (hair-like growths) have penetrated the cotton fiber wall and

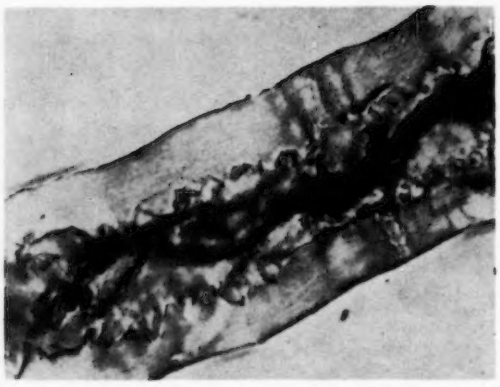

Fig. 4. Cotton fiber under fungus attack showing the penetration of the fiber wall by the fungal hyphae.

Fig. 5. Cotton fiber degraded by the action of the bacteria.

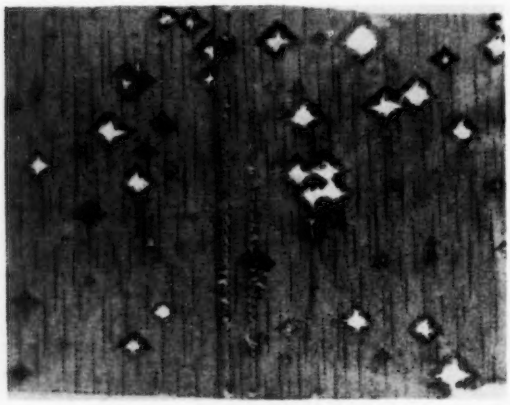

Fig. 6. The characteristic diamond-shaped patterns of fungus attack.

are growing profusely in the lumen of the fiber. It is unlikely, however, that the organisms ordinarily penetrate to the center of the fiber, because the fiber pores are too small to permit the passage of the hyphae, which average about 5 μ in diameter. The probable explanation is that the hyphae gained entrance to the lumen through chance cracks and broken fiber ends.

Bacteria have a less highly developed structure than fungi and operate largely as single cells. Bacterial attack is confined to the outside wall of the cotton fiber and proceeds inward to the lumen only when degradation is near completion. This is illustrated in Figure 5, which shows the outer wall of a cotton fiber that has been eroded by the action of bacteria on the surface.

The actual chemical breakdown of cellulose is effected by enzymes which the organisms release only in the presence of cellulosic materials. The reaction is a hydrolytic one, in which the insoluble cellulose chains are ruptured at the β 1, 4 glucosidic linkages to yield water-soluble sugars. The latter then diffuse into the microorganism to be further metabolized.

Early investigations by Pringsheim [253] indicated that cellulose was hydrolyzed by enzymes in the following manner:

$$\text{Cellulose} \rightarrow \text{Cellobiose} \rightarrow \text{Glucose}$$

The enzyme carrying out the first reaction was named "cellulase" and that catalyzing the second, "cellobiase." This concept was generally accepted until a few years ago. Recent chromatographic and electrophoretic studies indicate that the cellulase complex is composed of at least five enzymes [132, 182, 231], although some investigators have been unable to obtain these results with certain organisms [257, 323]. The enzymes have not been separated, and no information is available on their individual roles or their interrelationship in the metabolic scheme.

Glucose has been repeatedly shown as an end product of cellulose decomposition, but intermediate products other than cellobiose have not been found. It is not known whether or not glucose is produced in the absence of cellobiase. Siu has suggested that there may be more than one metabolic pathway for different organisms [300]. Some species, for example, may be able to utilize cellobiose as food, whereas other species can metabolize only glucose.

Microbial attack on textiles and related materials is easily recognizable. Commonly used criteria are a musty odor associated with mildew, and a characteristic staining caused by either the color of the organism itself or the reaction product of the enzyme excreted by the organism with a material which has been used in finishing the fabric. The colors of the stains vary from white to yellow, pink, green, brown, and red. If cellulolytic organisms are present, stains will occur in the form of diamond-shaped patterns whose diagonals correspond to the direction of the warp and filling in the fabric, as shown in Figure 6 [127]. This characteristic design is caused by

microbiological growth from the center of the attack, which occurs more rapidly along the warp and filling directions than across the open interstices. This results in the square or diamond form.

Distinction should be made between detection and identification of organisms. Detection involves merely determining the presence or absence of the microorganisms. Exact identification of the organism, on the other hand, is a highly complex problem, depending upon the morphological structure and physiological behavior of the organism. Precise and conclusive identifications are sometimes extremely difficult.

Bacteria are more difficult to identify than fungi because of the small size of the organisms involved and their more uniform shape and structure. Despite the recognized importance of bacteria in the textile field, difficulty in handling and observation has hampered investigators, so that the tendency so far has been to concentrate on the detection and identification of fungi.

Numerous methods are available for the qualitative evaluation of the power of the organisms to degrade cellulose. As a rule, the isolation of cellulose-destroying organisms does not present too great a problem. In instances where a dominant species is growing profusely on the surface of a fabric, a portion of the growth may be transferred to any number of the many standard microbiological culture media. The media are usually composed of finely divided cellulose mixed in an agar base [204]. The ability to decompose cellulose is indicated by the formation of cleared zones around the colonies of organisms on the agar plate.

Another method consists of submerging strips of filter paper in a mineral culture solution and inoculating the system with the organism from the textile [300]. A positive test for cellulolytic activity is the gradual disintegration of the paper. This disintegration is observed on occasional agitation of the container.

Other tests depend on the production of acids by microorganisms [279]. For example, a cellulose agar medium with a pH of approximately 8.4 and containing the red dye Aurin, which turns blue with increased acidity, is inoculated. In the presence of cellulose-destroying organisms, the agar plate becomes covered with blue zones around the areas of activity.

The microscope is also a useful tool in determining cellulolytic activity, and specific identification of the organism involved can at times be made. In conjunction with microscopic examination, several special stains are often employed for greater definition [76, 111, 251, 263, 300]. The microscopic techniques may be varied depending on the effects desired, i.e., a combination of swelling and staining or merely staining alone. Figure 7 shows cotton fibers previously swollen in alkali, then stained with Congo red. The undamaged fiber is stained a uniform pink. The two fibers which have undergone microbial attack show the characteristic disintegrated appearance. The fungal hyphae are stained a deep red.

Swelling agents alone also aid in microscopic examinations [111, 112, 251, 300, 316]. Such reagents

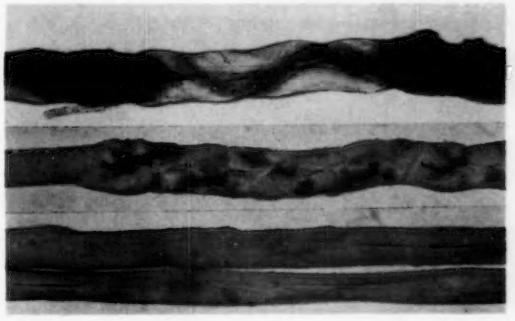

Fig. 7. Fibers stained with Congo red, showing, from bottom to top, no damage, slight damage, and serious damage.

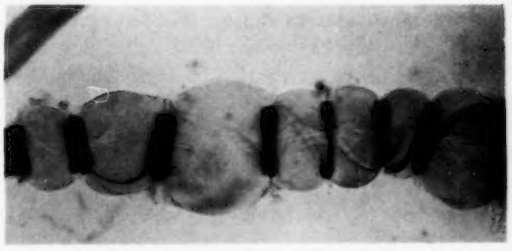

Fig. 8. Microscopical view of an undamaged cotton fiber swollen in carbon disulfide and sodium hydroxide.

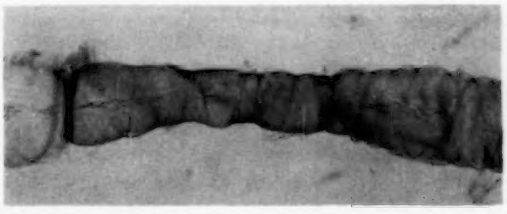

Fig. 9. Cotton fiber, damaged by microorganisms and swollen as in Figure 8.

as cuprammonium hydroxide and a mixture of sodium hydroxide and carbon disulfide, when acting on an undamaged cotton fiber, produce a swelling of the inner secondary wall. The primary wall, because of its limited elasticity, bursts into ring-like fragments which remain as bands around the fiber. As shown in Figure 8, a series of constrictions along the otherwise swollen fiber finally results. Figure 9 shows that this effect is not obtained with degraded fibers. The cuticle is digested away and the swelling of the secondary wall occurs without the attendant rings.

Another aid suggested for the detection of microbial growth on the surface of fabrics is ultraviolet light, because certain organisms show a characteristic fluorescence [74]. However, many microorganisms do not fluoresce, and it is not advisable to use this method as a general test for microbial damage on cotton [163].

Sunlight

The harmful effects of light on cotton have long been recognized. Since the early 1920's, photochemical degradation has been the subject of a large amount of work utilizing the sun itself or artificial light sources designed to approximate sunlight. Investigators agree that the extremely complex reactions involved are oxidative in nature, but the exact mechanism by which the action takes place is still obscure.

In order for light to cause a chemical change in any substance, the rays must be absorbed and be of sufficiently high energy content to change the molecular structure of the irradiated material. The amount of incident light absorbed by a fabric depends upon the yarn and fabric construction.

The effect of the physical structure on light susceptibility of fabrics has been investigated, and it has been shown that such factors as yarn twist, yarn crimp, ply, and weave have an important bearing on the amount of degradation occurring on exposure [146, 147]. Heavy fabrics, closely woven from highly twisted yarns, are the least deteriorated by light. The extent of the chemical change produced also depends on the frequency of the radiation absorbed. Higher frequencies (shorter wave lengths) produce a greater change because they furnish greater amounts of energy per unit of radiation.

Greige and bleached cottons differ in their rate of photochemical degradation [146, 184]. In sunlight exposures, bleached cottons deteriorate more rapidly than greige fabrics. The two possible explanations for the greater rate of degradation of bleached fabrics are that the foreign material on the greige cotton acts as a filter to cut down the damaging light rays or that bleaching of the cotton causes a weakening of the cellulosic linkages, which are then more easily broken by the action of light.

The ultraviolet region with wave lengths between the limits of 2,500–4,000 Å is the most degrading to untreated textiles [348]. The rays of this region possess high energy content per unit of radiation, and their absorption by cellulose produces more rapid degradation than equal periods of exposure to other parts of the spectrum. Investigations on the effects of radiation from sunlight have, therefore, been concerned primarily with the ultraviolet region. Experiments have shown that cotton suffers greater deterioration from ultraviolet light acting alone than from the same amount of ultraviolet radiation accompanied by light in the red-orange portion of the spectrum [69]. The effect of light on ozone formation has been presented as an explanation of this. The most effective wave length for the conversion of oxygen to ozone is 3230 Å, in the ultraviolet portion of the spectrum; on the other hand, the most effective deactivating (from ozone to oxygen) wave length is 6010 Å, lying in the orange region. Thus, with orange and ultraviolet light both present, ozone may be deactivated as soon as it is produced.

Further insight into the problem has been given by Egerton [99, 101] who, from considerable experimental data, has postulated two probable mechanisms of action based on the theory that the effects obtained depend upon the particular region of the ultraviolet in which the exposure is made.

In the short wave ultraviolet region (2537 Å), the effect is one of photolysis, in which the light absorbed by the cellulosic material produces a disruption of the carbon–carbon and carbon–oxygen bonds. This action can take place in the presence or absence of oxygen. In either instance, upon subsequent exposure to oxygen the degradation products may undergo further oxidation. This process can also occur in the near ultraviolet (3400 Å) and the visible range (4000–7000 Å), but at a reduced rate, since smaller amounts of energy are received by the cellulose.

In the near ultraviolet and visible range, the effect is one of photosensitization, in which certain dyes

and pigments are capable of absorbing light from which energy is made available for the degradation of the cellulose. The light energy absorbed by the dye is transferred to the oxygen in the surrounding atmosphere, yielding activated oxygen or ozone. The activated oxygen then reacts with water vapor to produce hydrogen peroxide. Thus, the degradative process of dyed cotton can be ascribed in part to oxidation of cellulose by activated oxygen and/or hydrogen peroxide.

Light is believed to break the molecular chain of cellulose into shorter units and to weaken the glucosidic linkages so that they are more readily attacked and ruptured by oxygen [161]. The rate of the reaction is increased when moisture is present. The breakdown products obtained possess the properties of a reducing type of oxycellulose [254]. Only slight degradation of cotton occurs when fabrics are exposed in inert atmospheres of carbon dioxide or nitrogen, both in the presence and absence of water vapor. However, on subsequent exposure to oxygen in the absence of irradiation, rapid deterioration occurs. The rate of this oxidation is greater at elevated temperatures.

Certain dyes and pigments reduce light degradation by reflecting or absorbing harmful wave lengths, while others accelerate the deterioration process. Vat dyes were first recognized as sensitizers of photochemical degradation. Since this discovery, numerous studies have been carried out, and it is now known that a large number of dyes other than vats, and certain pigments such as zinc oxide and titanium dioxide, function as photosensitizers when applied to cotton fabrics [18, 26, 100, 165, 197, 280, 327, 342]. The following conclusions are in general true for the different classes of dyes used on cotton [18].

1. Vat dyes, because of their fastness, are usually used on fabrics which will be subjected to weathering. There are many dyes in this class that enhance the resistance of cellulose to deterioration. Photochemical or sensitizing activity is confined to the yellow, orange, red, and brown dyes.

2. Sulfur dyes, like the vats, show a correlation between the color of the dye and its photochemical action. The blue and green dyes of this class are less active than the yellows and browns, some of which exert a pronounced sensitization.

3. Basic dyes, which are fugitive to light, act as sensitizers, but there seems to be little or no relationship between color and increased activity. Violets and greens, as well as the yellow and orange dyes, may accelerate deterioration.

4. Direct dyes have not been fully investigated, but of those tested, primuline (C.I. 812) is the only one which exhibits a sensitizing effect. This activity is thought to be a function of the structure of the dye molecule, which, unlike the majority of other direct dyes, is a thiazole and not an azo dye. Evidence that the structure is responsible for the degrading action has been gained in the following manner. The amino groups in primuline were diazotized and coupled on a fiber with a phenol to yield a direct dyeing which, upon exposure to light, exhibited little or no acceleration of photochemical oxidation. The result suggests that direct dyes do not accelerate photochemical degradation, and that the sensitizing activity of the thiazole nucleus has been reduced by the introduction of an azo linkage into the primuline molecule.

The sensitizing effects of the vat and sulfur dyes on cotton are decreased appreciably by treating the fabric after dyeing with a copper-salt solution [18]. These results are surprising, since copper is known to accelerate the photodegradation of undyed cotton. Small quantities of iron, and of some other metals, also reduce the rate of photochemical degradation.

Photo-oxidation studies on simple compounds structurally related to cellulose have given some insight into the mechanism of photosensitization [12]. These compounds ranged from simple primary and secondary alcohols through glucosides and disaccharides to polysaccharides. The results of this work indicate that the tendering process begins when the photo-excited dye molecule takes a hydrogen atom from the cellulose molecule. Oxygen adds to the cellulose molecule to yield a peroxy radical. The site of the initial attack determines one of two later reactions. In one case decomposition of the peroxy radical will cut the cellulose chain immediately; in the other, a carbonyl group may form within the chain. If a carbonyl group forms, the cellulose has a weak link. Later exposure to alkali such as in laundering breaks the chain at this point.

Several approaches might be taken to overcome this sensitizing activity. These would involve the development of methods either to prevent the formation of excited dye molecules or to cause the excited dye molecules to lose their energy in other ways than by attack on cellulose molecules [12].

Airborne Acids

In industrial and thickly populated areas, traces of acids or acid-forming substances such as sulfuric acid or sulfur dioxide in the atmosphere often contribute to the deterioration of exposed cotton fabrics [254, 348]. The source of these acid-forming substances is usually the combustion of fuels used for household heating or industrial heating and power.

These acidic constituents behave as aerosols and are deposited on exposed fabric in several ways. Precipitation (rain, snow, fog, or dew) tends to form around such particles as a nucleus and conduct them to the fabric. Gravity, electrostatic attraction, and direct interception also play a part in the deposition of particles on the fabric.

The mechanism of attack, as shown in Figure 10, is a simple hydrolysis wherein the cellulose chain is attacked at the glucosidic linkage. This causes a decrease in the degree of polymerization of the fiber and results in lowered breaking strength and increased fluidity.[5]

Some indication of the significance of this type of degradation is derived from an analysis of the data collected from a series of outdoor exposure tests in a highly industrialized area [254]. As illustrated in Figure 11, the breaking strength of the fabric, pH of the rain, and pH of the atmosphere were measured monthly over a 1-yr. period. The maximum attack took place during the winter months and the minimum deterioration occurred in the spring and fall. The probable explanation is that during the latter seasons neither photochemical degradation nor the action of corrosive atmosphere is at a maximum. Also, the heavy industrial fogs which often occur during the winter months are quite acid. Contributing factors to both fog and acid formation are undoubtedly the lower winter temperatures, favoring greater condensation of volatile acids, and the much greater consumption of fuel in winter than in summer.

Alternate Wetting and Drying

At least a portion of the deterioration normally attributed to weathering is caused by the alternate wetting and drying of fabrics. This has been established by controlled studies in which fabrics were exposed to this action under conditions analogous

[5] Fluidity is the reciprocal of viscosity and is measured by dissolving the cellulose in a cuprammonium hydroxide or a cupriethylene diamine solution and measuring the viscosity by the orifice or falling-ball method.

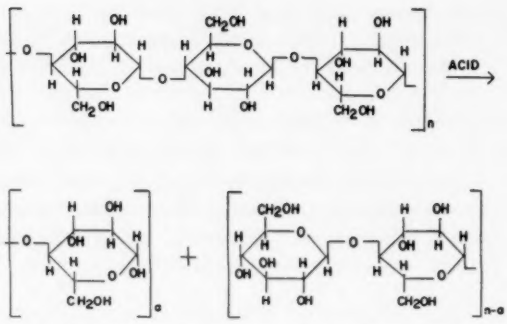

Fig. 10. The hydrolysis of cotton cellulose by acid.

to those existing out-of-doors but without the effects of other interfering factors; for example, sunlight and airborne acids [47, 48, 49, 212]. The results of these experiments indicate that continuous evaporation of a liquid at a wet-dry interface on a fibrous material in contact with air is accompanied by chemical modification of either the liquid or the fibrous material, depending on their natures. The effect can best be observed in a "wicking" test where the lower end of a strip of purified fabric is dipped in distilled water and capillary action causes the water level to rise on the fabric. When the evaporation of water has continued for some time, a brown line is observed at the point which marked the highest rise of water on the fabric. If the experiment is carried out at room temperature, no loss in the breaking strength of the fabric will occur at the interface. Elevated temperatures over prolonged periods, however, will produce losses.

The brownish substance, which is water soluble and exhibits a pronounced fluorescence under ultraviolet light, was identified as an oxidized cellulose of the mildly reducing acidic type [47]. The occurrence of this phenomenon is prevented by the rigorous exclusion of oxygen, and this is good evidence of the oxidative nature of the reaction. The identity of the oxidant, however, is not known. This brown line reaction on cellulosic materials is an example of a general phenomenon. Other fibers and liquids also participate in this oxidative type of reaction [281]. With organic liquids, such as n-pentane, the reaction appears to be confined to the liquid; with water, a modification of the fiber occurs.

This same action probably takes place in a fabric exposed to weathering. Over prolonged periods of service, the entire fabric would presumably be weakened by repeated wetting and drying cycles. Figure

12 is a photograph of a window shade which was frequently wetted by rain over a period of three years. At the end of this time it could be torn very easily in the interface region. In most instances the area of attack is not so well defined, and evaluation of the relative importance of this mechanism is difficult. In tropical areas, there are seasons of the year at which frequent rainstorms followed by periods of drying would tend to increase the relative importance of this type of deterioration.

Abrasion

"Atmospheric abrasion" can take place in either or both of two ways: by the action of an abradant such as sand or dust in the air or by the rubbing of the fabric on itself or on its surroundings, caused by movement due to wind action. The total amount of damage caused by abrasion from wind-carried particles is quite small, even in such areas as the southwestern part of the United States, where wind erosion produces sand and dust storms.

The importance of self-abrasion, flexing, and the rubbing of the fabric on its surroundings can be seen in any application of awnings, tents or tarpaulins.

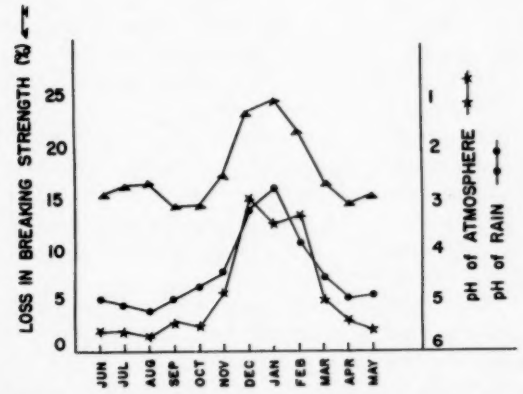

Fig. 11. Effect of outdoor exposure in a highly industrialized area on cotton yarn breaking strength.

Protective Treatments

An ideal weather-resistant finish should protect the fabric from the degrading action of sunlight, inhibit microbial growth and deterioration, and prevent damage by moisture and atmospheric fumes—all in the same treatment. The finish should also be permanent and economical, with no adverse effects on the physical properties or appearance. At present, no one single treatment or combination of treatments meets all of these exacting requirements. Those which are available vary widely in the type and degree of protection afforded.

Since the ideal is not yet available, the finisher is faced with the task of selecting the single treatment or combination finish which most nearly meets the end-use requirements. Selection of the optimum finish for a particular end use is more of a problem than might first be realized, because cotton fabrics are used in such a wide variety of end products which are in turn subjected to such a wide range of weathering conditions. Depending on use and geographical area, a particular treatment may be suitable for a fabric in one location but not in another. For example, in arid desert regions tents or tarpaulins would need protection against sunlight and perhaps abrasion from wind-blown sand or dust, but not mildew or rot. In contrast, in shaded jungle areas they would require treatments highly resistant to microorganisms, but would need little, if any, resistance to sunlight.

The following paragraph lists a number of classes of possible treatments, many of which are now being used commercially to improve cotton's weather resistance.

Mildew and Rot Prevention

Siu divides the treatments which are used for mildew and rot prevention into three classes [300].

1. Physical barriers or coatings, which prevent access of the organism to the substrate.

Fig. 12. A photograph of a window shade which was frequently wetted by rain over a three-year period.

2. Toxic inhibitors or fungicides, which either inhibit the further development of the organism or bring about death.

3. Chemical modifications of the fiber, which render the chemical groups on the cellulose molecule inaccessible to attack by the organism.

Physical barriers. Microbiological degradation of cotton fibers, as previously described, requires direct contact between the organism and the fabric. Inert protective coatings should therefore increase the resistance of cotton to microorganisms.

Coatings are applied by "knifing" or spreading, in which the substance is flowed on the fabric and spread by means of a doctor blade, or by a calendering operation such as that commonly used for applying rubber or similar finishes [288].

Pine tars and coal-tar creosotes have been used for years by fishermen to impart some fungal resistance to net and ropes. Toxic substances in these materials also contribute to their protective action. The objections to creosotes are numerous—odor, stickiness, increased flammability, and stiffening make them undesirable. In addition, creosote and pitch paints in high concentrations increase photochemical deterioration of fabrics [57]. Another process which can be cited as an example of the barrier mechanism is the coating of cloth with plasticized pitch and emulsions of used gear oils, called bitumen. This material alone, however, is not very effective and for best results must be applied in combination with fungicides [300].

Fabrics coated with rubber, parraffin, chlorinated paraffin, and vinyl polymers show considerable resistance to microorganisms when properly applied [156, 176, 300, 319, 324]. However, in many instances barrier coatings are either not sufficiently continuous or they adversely affect other textile properties. Care must also be exercised when plasticizers are used in coatings. Many plasticizers, particularly the fatty-acid derivatives, are conducive to attack by microorganisms, but resistant types are available [1, 51, 61, 300].

Toxic inhibitors. The second broad approach to prevention of microbiological attack on textiles is the application of compounds which act as poisons. Toxic inhibitors or fungicides either inhibit the microorganisms from further development or bring about death. The end result is conditioned by such factors as pH, composition of the medium, temperature, and other environmental factors. Frequently, the difference in toxicity is simply a matter of inhibitor concentration.

Compounds having widely different properties and chemical structures inhibit growth, and slight differences in molecular structure often bring about vast changes in toxicity. A certain amount of correlation has been noted between chemical structure and toxicity [314]. In a homologous series of derivatives with changes only in hydrocarbon chain length, the lowest members of the series have little effect. With increasing chain length, the toxicity rapidly rises to a maximum and then falls off rapidly.

Numerous theories have been proposed to explain the action of inhibitors, but none has been substantiated [300]. It is believed that fungicides must be very slightly water soluble to be effective toxic agents. High water solubility tends to increase the toxic characteristics of some inhibitors, but there are a number of exceptions. For application to cotton fabrics where durability to weathering is required, any appreciable water solubility is undesirable because of the loss of the agent by leaching.

Toxic inhibitors include many classes of chemical compounds with different degrees of solubility in solvents and water. They may be applied to the fiber, sliver, yarn, or fabric at sizing, dyeing, or other stages of manufacturing. For outdoor use, they are usually applied in conjunction with other protectants such as resins, waxes, or other hydrophobic materials. When used alone, the most effective fungicides are removed with comparative ease from the fabric, presumably because of their water solubility or, in the case of organic inhibitors, of the water solubility of the products formed by their breakdown on the fabric [267].

The majority of the commercially available fungicides are applied by one of four methods, selected with consideration of the intended use [300].

1. Single bath method. The inhibitor is dissolved in an organic solvent and is padded on the cloth. This gives good penetration and is quite rapid. Disadvantages of using organic solvents in the textile industry include toxicity, fire hazard, cost, and difficulty of recovery.

2. Single-bath emulsion. The inhibitor is emulsified in water, usually with the aid of a surface active agent, and the emulsion is padded on the cloth. This method overcomes the disadvantages of the solvent method, but may be characterized by nonuniformity and poor penetration.

3. Two-bath method. This treatment takes place in two steps. First, the water-soluble sodium or ammonium salt of the inhibitor is padded on the fabric. Then acid is padded on to regenerate the original insoluble compound. The acid bath is usually a solution of a waterproofing compound, acidified with acetic acid. Instead of alkaline and acid solutions, the two baths may contain the separate halves of the inhibitor molecule, and the two radicals are made to react on the fibers themselves.

4. Vehicle carrier method. This method involves application of the toxic inhibitor in various vehicles such as oils, pine tar, rubber, pyroxylin, and wax paste. These may be applied as coatings using a calender or spread by knife.

Toxic inhibitors in use at present may be classified into five groups according to their chemical composition [300]: (1) copper compounds, (2) non-copper organometallic compounds, (3) phenolic compounds, (4) quaternary ammonium compounds, and (5) sulfur-containing organic compounds.

Copper derivatives are used extensively as fungicides, since copper ions are toxic to cellulolytic microorganisms at concentrations as low as one part per million [256]. Copper inorganic compounds, however, are limited in use because of their adverse effects and lack of permanency on textiles. Replacement of these by copper organic salts and other organic compounds occurred rapidly after the beginning of World War II. None of the copper derivatives can be used in conjunction with rubber coatings, since copper accelerates deterioration of rubber.

Probably the compound most widely used is copper naphthenate [36, 42, 121, 137, 170], a product of the reaction between a copper salt and "naphthenic" acids found in high boiling petroleum fractions. This derivative is a potent mildew inhibitor. The naphthenic acid radical itself possesses strong inhibitory action and no doubt contributes to the over-all protective properties of the salt. There are disadvantages connected with the use of copper naphthenate. When used alone and exposed to weather, the compound undergoes an appreciable amount of hydrolysis. The actual copper content of the fabric apparently does not change, but the benzene-soluble copper fraction is converted to an insoluble form. The latter consists of the basic naphthenate and basic copper oxides which are less effective than the naphthenate itself. The greenish color of copper naphthenate is a decided obstacle when white or colored fabrics are desired. The compound has an unpleasant odor and is an irritant to human skin when the copper concentration exceeds 1%. There is also strong evidence that copper naphthenate catalyzes the photochemical breakdown of fabrics [46]. This disadvantage, however, can be overcome by the addition of screening pigments and waxes to the coating [33].

Copper hydroxynaphthenate is often used as a diluent of the naphthenate in equal concentration to reduce odor and crocking and conserve naphthenic acids. The commercial product is not a chemically pure derivative and usually consists of a solution of copper naphthenate with excess alkali. It possesses a lighter color but has a much lower order of effectiveness than the naphthenate [1, 35].

The application of copper-8-quinolinolate, the copper salt of 8-hydroxyquinoline, to cotton fabrics imparts considerable resistance to microorganisms [1, 35, 44, 175]. This inhibitor is a practically odorless, light yellowish-green compound having a high degree of insolubility in both water and common organic solvents. The insolubility of this fungicide in most solvents and its high cost have been major drawbacks for application on textiles. Solubilized preparations of this compound in oleic acid, linseed oil, castor oil, or cottonseed oil are now available which show excellent results as an inhibitor for many uses [300]. The permanency of the fungicide is increased by bonding with surface resins. The quinolinolate does not appear to accelerate photochemical degradation.

A solubilized copper complex of N-nitroso, N-phenyl hydroxylamine, commonly known as copper cupferron, also shows good fungicidal properties. Its previous limitations were high cost and insolubility, both of which have been corrected [190]. In activity it is comparable to solubilized copper-8-quinolinolate. The compound is applied from solvent solution, water dispersion, or in combination with water repellent materials. Cotton fabrics treated with copper cupferron do not have the characteristic blue or green copper color but are an off-white to grayish-green color at concentrations normally required. The finished fabric has no odor and the product does not accelerate photochemical degradation [190].

Copper resinate and copper oleate are used occasionally as preservatives, but are inferior to the aforementioned compounds [1, 219, 328]. Resin acids are found in tall oil, a waste product of the

Kraft pulp industry. The resinate is relatively cheap and resistant to leaching but imparts brittleness and stiffness to a fabric and gives little lubricating action. Copper oleate, a product from the reaction of oleic acid and a copper salt, is difficult to apply and also imparts stiffness. The compound is also claimed to increase the light tendering of cotton fabrics [34].

Of the metallic-organic inhibitors which do not contain copper, the main ones which have been in use are mercury derivatives [1, 35, 145]. In contrast to most of the copper compounds, mercury fungicides are colorless and odorless and can be used on white fabrics. They are, however, more expensive and considerably more toxic to man. Derivatives of the phenyl- and pyridyl-mercuric type have been the most popular [80]. The phenyl mercurials are stable under ordinary conditions. However, gradual decomposition takes place on long standing under alkaline conditions, in sunlight or in the presence of reducing agents, and many of them are not resistant to leaching [300]. Phenyl mercuric naphthenate is probably the most effective of the commercially available phenyl mercuric compounds, and pyridyl mercuric acetate, chloride, and stearate the most efficient of the pyridyl mercuric agents [1].

The zinc inhibitors are less toxic than the mercury compounds. Zinc naphthenate and zinc dimethyldithiocarbamate are sometimes used when a colorless preservative treatment is desired [36, 121, 137, 190]. Zinc naphthenate is only about half as effective as the corresponding copper derivative, and its poor weathering characteristics, odor, and stiffening effects on fabrics limit its use to certain applications [190]. Zinc dimethyldithiocarbamate is apparently a more potent inhibitor than zinc naphthenate but is lost during weather exposure tests [35].

Organo-tin derivatives have also been investigated for possible use as fungicides on textiles [172]. Cotton fabrics treated with diethyloctyltin acetate and diethyllauryltin acetate show a high degree of resistance to microorganisms in soil burial tests [172]. Another compound of this type, bis (tri-n-butyl-tin) oxide has been offered for use as a mildew-resistant treatment for cotton, but no published information is currently available on which to judge its effectiveness [258].

The phenolic derivatives such as the polychlorophenols, diarylmethanes, and arylamides are no longer widely used as fungicides, but several are still important as toxic inhibitors. They are usually applied in the form of the soluble sodium salt or as an emulsion of the parent compound [220, 221].

The most widely used and most active of the chlorinated phenols from the standpoint of inhibitory action is pentachlorophenol [1, 300]. Its greatest disadvantages are poor resistance to leaching and an accelerated tendering of the fabric by sunlight. These effects are improved by joint application of the fungicide with thick finishes for fire, water, and weather resistance [43]. When applied in conjunction with other finishes, it undergoes some volatilization, especially if the fabric is dried at elevated temperatures. The compound is also an irritant and is seldom used on fabrics which will be in contact with the skin.

G-4 is the commercial abbreviation for 2,2′ dihydroxy, 5,5′ dichlorodiphenylmethane, which was developed as a fungicide during World War II. This diarylmethane is a symmetrical condensation product of formaldehyde and *p*-chlorophenol. It is far less toxic and volatile than other phenolic derivatives and is compatible with ordinary treatments for water repellency [300]. The compound apparently does not accelerate photochemical degradation, although some figures have been produced suggesting rapid destruction by weathering [35].

Salicylanilide is the most important of the arylamide inhibitors [108, 109, 148, 173, 203]. Like most of the phenolic derivatives, this compound is not durable under outdoor conditions and therefore has found its greatest use for preservation of fabrics for shipping and storage where the fabric is not exposed to weathering processes. The durability of this fungicide is improved by applying it in conjunction with wax-and-aluminum-salt water repellents and other finishing treatments [120, 121].

A derivative of a polyhalogenated phenol, trimethyloctadecylammonium pentachlorophenate, was used extensively at certain periods of World War II in the preservation of military fabrics. Tests have indicated that it is resistant to leaching but accelerates photochemical degradation [22]. The reaction products of quaternary ammonium compounds with phenolic derivatives have been patented, and such compounds as cetylpyridinium bromide and the methosulfate of methyl diethylaminoethylstearamide are claimed to possess a greatly reduced solubility and consequently a greater durability on fabrics than the phenolic compounds alone [311].

Quaternary ammonium naphthenates have been

found useful in the mildewproofing of bed linens or clothing items where a given amount of the fungicide is to be added to the fabric by means of a laundry wash wheel or similar apparatus [190]. These compounds are used for these purposes because of their low toxicity, lack of color, low odor, and their sustained activity in soil burial as well as pure culture tests.

Only a few of the sulfur-containing organic compounds have been tested as toxic inhibitors. The aforementioned zinc dimethyldithiocarbamate [35] and 2-mercaptobenzothiazole [37, 283] are the most important fungicides of this type.

The ultimate test as to the usefulness of a given treatment is its performance under conditions of actual use. Studies of this nature have been carried out in which cotton fabrics of different weights were treated with various fungicides and exposed in different ways in tropical areas [22]. The inhibitors were applied to the fabric by various methods and jointly with other treatments such as dyeing, water-repellency, light-screening, and flameproofing. From these tests the following conclusions were drawn.

1. Fungicides satisfactorily resistant to sunlight: copper naphthenate (with screening pigment), copper-8-quinolinolate, phenylmercuryethanolamine lactate, and pyridylmercuric stearate.

2. Fungicides satisfactorily resistant to soil burial: copper naphthenate, copper hydroxynaphthenate, copper-8-quinolinolate, pyridylmercuric chloride, pyridylmercuric stearate, cuprammonium fluoride, and 2,2′-dihydroxy, 5,5′-dichlorodiphenylmethane.

Table VI gives a comparison of toxic inhibitors evaluated by means of soil burial tests on cotton duck [1]. On the basis of this data, the naphthenates, the pyridyl mercuric derivatives, zinc dimethyldithiocarbamate, pentachlorophenol, and 2,2′-dihydroxy, 5,5′-dichlorodiphenylmethane appear to be the most effective.

From the standpoint of all-around performance, copper naphthenate (with screening pigment), copper-8-quinolinolate, and copper cupferron (the latter two are not shown in Table VI) are probably the best available fungicides for the mildew- and rot-proofing of cotton tentage. The pyridyl mercuric compounds are potent inhibitors but are toxic to

TABLE VI. Relative Effectiveness of Fungicidal Agents on 10-Ounce Cotton Duck*

Inhibitor	Concentration, %	Residual strength after soil burial		
		3 weeks	6 weeks	9 weeks
o-Phenylphenol	3.0	0	0	0
2,4,5-trichlorophenol	2.0	100	26	0
2,4,6-trichlorophenol	3.0	0	0	0
2,3,4,6-tetrachlorophenol	2.0	100	44	0
Pentachlorophenol	1.0	83	46	38
Chloro-2-phenylphenol	3.0	100	0	0
2-chloro-4-phenylphenol	1.5	0	0	0
2-bromo-4-phenylphenol	1.5	39	0	0
2,2′-dihydroxy, 5,5′-dichlorodiphenylmethane	1.0	100	93	59
Salicylanilide	1.0	86	40	0
p-Nitrophenol	1.5	36	0	0
Phenylmercuric acetate	1.5	97	0	0
Phenylmercuric salicylate	1.5	76	0	0
Phenylmercuric hydroxide	1.5	99	48	0
Phenylmercuric oleate	1.5	78	0	0
Phenylmercuric naphthenate	1.0	75	66	45
Phenylmercuric acetoxyoctadecanoic acid	3.0	90	0	0
Phenylmercuric triethanolamine lactate	3.0	36	0	0
Pyridylmercuric chloride	1.0	100	73	43
Pyridylmercuric stearate	1.0	91	89	38
Pyridylmercuric acetate	1.5	97	77	56
Mercaptobenzothiazole	1.5	100	72	0
2,3-dichloronaphthoquinone	1.5	79	0	0
Zinc naphthenate	1.5	91	74	60
Zinc dimethyldithiocarbamate	0.5	98	81	69
Copper naphthenate	1.0	94	83	61
Copper hydroxynaphthenate	1.0	70	54	14
Copper oleate	1.5	45	0	0
Untreated		0	0	0

* Source: National Bureau of Standards, Misc. Publ. 188(1).

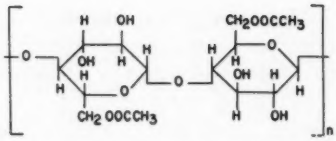

Fig. 13. The formula for acetylated cellulose molecule with a degree of substitution of 1, or 20% acetyl content.

humans. For lightweight fabrics and also for fabrics where stickiness is undesirable, copper-8-quinolinolate, 2,2′-dihydroxy, 5,5′-dichlorodiphenylmethane, and quaternary ammonium naphthenate appear to be the most suitable.

The use of a single inhibitor has shortcomings because certain species of fungi are or may become immune to particular fungicides. The combination of two or more fungicides with contrasting properties has been shown to enhance the action of individual inhibitors [33, 108, 335].

Chemical modification. Chemical modification refers to the treatment of cotton fiber, yarn, or fabric with specific chemicals to change its chemical composition without destroying the fiber form. This differs from the chemical modification of purified cellulose, made from cotton linters, wood, or fibrous agricultural wastes, to obtain a chemical compound that can be dissolved and then spun or cast into materials like rayon or transparent sheeting. Most chemically modified cottons which have been studied to any extent in this country are partial modifications, in which the hydroxyl groups in the amorphous portions of the fiber and those accessible groups presumably on the crystallite surfaces are reacted [82, 95, 135].

Chemical derivatives of cellulose are resistant to cellulolytic organisms, but not to the noncellulolytic. In other words, they protect cellulosic fabrics from deterioration, but are not in themselves fungicidal [80]. The protection obtained is attributable to one or both of two factors: blocking, the addition of a substituent group at the place in the cellulose molecule where the biochemical attack of the organism's enzyme would take place; and steric hindrance, the prevention of the expected reaction due to the changed spatial arrangement of the atoms in the modified cellulose.

Chemical modification of cotton as a rot-preventive treatment offers a number of advantages over the use of materials which work through toxic inhibition. The effectiveness of the modification rests on the inability of secreted enzymes to attack the modified cellulosic substrate. Because the chemical substituent is an integral, insoluble part of the cotton fiber, it can't wash out. On the other hand, fungicides, to be effective, must have a degree of water solubility, and are thus inherently less durable. Unlike inhibitors, the resistance of chemically modified fibers does not depend on poisoning the organism and therefore offers little danger of toxicity to man. In addition, the cellulose derivatives are resistant to all cellulolytic organisms, whereas inhibitors often show differential tolerances and a specificity for certain organisms.

The commercial applications of chemically modified cottons as a preventive method for rot have been limited by a number of disadvantages. These are increased cost and difficulty of application over conventional fungicidal treatments, high add-on weight, and losses in tear strength and abrasion resistance of the fabric [121].

Acetylation.—Cotton may be acetylated in the fiber, yarn, or fabric form. In this process, cotton is reacted with a mixture of glacial acetic acid and acetic anhydride, with perchloric acid being used as a catalyst. The formula for the acetylated cellulose molecule with a degree of substitution of 1, or 20% acetyl content, is given in Figure 13.

Partially acetylated cotton fabrics are highly resistant to deterioration by microorganisms [95, 135, 319]. Sandbags made of acetylated cotton have withstood two years of exposure at New Orleans [135]. Acetylated cotton with a 30% acetyl content or a degree of substitution of 1.4 per anhydroglucose unit has withstood soil burial exposure in Panama for 30 and 50 weeks with little or no loss in strength [300].

Fully acetylated cotton with an acetyl content of 36–45% has also been prepared [67]. The procedure is similar to that employed for partial acetylation. The cotton is reacted with acetic anhydride in a nonswelling diluent, amyl acetate, and perchloric acid is used as a catalyst. Under carefully controlled conditions for maximum reactivity, the product shows the high level of resistance to microorganisms which may be expected from its composition.

Cyanoethylation.—Another chemical modification that has received considerable attention in recent years is cyanoethylated cotton [78, 79, 139]. As shown in Figure 14, acrylonitrile is reacted with cotton under alkaline conditions to yield a cyanoethyl cellulose ether. The extent of the reaction is con-

ditioned by the thoroughness of the pretreatment and concentration of the sodium hydroxide solution, the temperature of the acrylonitrile, and the time of contact with acrylonitrile. This process is carried out in a closed system because of the toxicity of the acrylonitrile and its explosive properties when mixed with air.

Cyanoethylated cotton, like acetylated cotton, has excellent resistance to cellulolytic microorganisms [79, 139]. Cyanoethylated cotton duck, with a nitrogen content of 3–3.5% (0.4 cyanoethyl groups per anhydroglucose unit), has withstood soil burial exposure for periods extending over 6–12 months without significant loss in strength [79]. Cotton yarns and fabrics modified by this method also have other advantageous properties such as increased heat resistance, and are more resistant to degradation by organic and mineral acids [79]. Both the cyanoethylated and the acetylated product, however, are just as susceptible as untreated cotton to sunlight degradation.

Cross-linked cottons.—Cellulose-reactive resin precondensates such as the cyclic urea formaldehyde and melamine types are applied to billions of yards of cotton fabrics each year to impart crease resistance and wash-wear properties. Cottons treated with these reactive compounds are also resistant to microbiological degradation [80, 341]. Fabrics are usually treated by immersion in an aqueous solution of the resin precondensate and an acid-forming catalyst. The fabric is then dried and cured. At one time there was considerable controversy as to the exact mechanism of action. Some thought the polymerized precondensates acted mainly as physical barriers, while others maintained that a chemical reaction took place. Today it is generally accepted that the precondensate is involved in a chemical reaction with cellulose, probably by the formation of ether cross-linkages [80, 130]. This is indicated by the insolubility of the treated fiber in cellulose solvents such as cuprammonium hydroxide.

In a recent study, it has been found that the microbial and weather resistance of a cotton fabric may be improved by the application of a formic acid colloid of methylolmelamine [41]. The protection afforded is much better than that ordinarily obtained by reacting the cotton with resin precondensates in the conventional manner. Photomicrographs show that the colloids are deposited in the outer portion of the fiber cell wall, whereas the conventional process deposits resin about halfway through the cell wall.

Other derivatives of cellulose.—A reaction is thought to take place when cotton cellulose is heated with a dilute solution of copper formate. Initial studies indicate that this treatment imparts good microbiological protection to fabrics and does not accelerate photochemical degradation [4]. The actual mechanism of the reaction is not known, but cellulose solubility tests in cuprammonium hydroxide and cupriethylene diamine give evidence that the copper in some form is chemically bound to the cellulose rather than physically deposited.

Other chemical derivatives of cellulose have been prepared [66, 80, 133, 259, 300, 322]. As previously mentioned, practically all of them show some resistance to microorganisms, depending on the degree of substitution. Like the cross-linked cottons, several of these modifications are dual-purpose treatments, and many of them were investigated for reasons other than imparting resistance to microbial degradation. For example, the urea-phosphorylation method and the titanium-antimony complex treatment were patented primarily for flameproofing purposes, but they also make the cotton fiber rot resistant [22, 80, 300].

Resistance to Sunlight

The light sensitivity of fibers is a function of their capacity to absorb the energy of light rays. When a beam of light falls on the surface of an object, it may be reflected, transmitted, or absorbed. A combination of all three can and does take place in most instances. Textiles which reflect light are more resistant to the sun's rays than those which are dull and absorb light. For example, the extra long staple

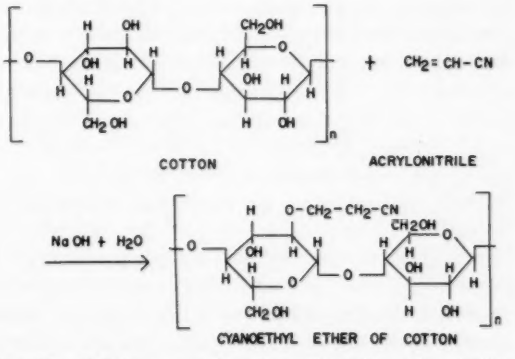

Fig. 14. Cellulose reacted with acrylonitrile under alkaline conditions to yield a cyanoethyl cellulose ether.

varieties of cotton such as Supima and Egyptian are more resistant than less lustrous cottons [284].

Certain inorganic and organic compounds, when applied to cotton fabrics, have the property of reducing the amount of degradation caused by sunlight exposure. Protection is attributed to their reflective and absorptive capacities, but absorption and reflection are rarely, if ever, perfect in actual materials or surfaces [106]. When a surface absorbs radiation, the molecules are raised to a higher energy level. An excited molecule may dissipate the absorbed energy in a number of ways. It may dissociate, lose energy by collision, fluoresce, or react with other molecules at collision.

Pigments. The light resistance of cotton fabrics is increased by the application of certain inorganic or organic pigments. The protective effect of pigments has been explained in several ways. Race [254] suggests two possible explanations for the protective action of chromic oxide: that it is a purely physical mechanism in which the chromic oxide absorbs radiation of wave lengths slightly below 3,500 Å, which are known to cause photochemical tendering of cellulose; or that the chromium forms covalent linkages with the hydroxyl groups of the cellulose and prevents the oxidative reactions which would otherwise occur. Neither hypothesis, however, has been fully explored or proven. Heffner [156] attributes the protection to a "screening out" of the major destructive bands of solar radiation in the 2500–3500 Å range.

Today, approximately 4,000 different pigments are available to the coatings manufacturer. They range from simple carbon black to complex organic compounds. Combinations of three or more pigments are often used in a single formulation. They are applied by chemical precipitation or by impregnation into the fabric, and often in conjunction with coatings. Best protective results are obtained with the latter method. In some instances, vat dye pigments are bound to the fabric with resins; they frequently have much better lightfastness used in this fashion than if dyed as conventional vat colors [333].

Data are lacking on the protective effect of many individual pigments. In recent studies [64, 65], the effectiveness of 126 pigments applied in conjunction with alkyd resin coatings to a canvas previously treated with urea-formaldehyde and copper-8-quinolinolate were investigated. The pigment portion of the coating was found to have an important bearing on the weather-resistant properties of the canvas to which it was applied. Depending upon the pigment used, effects ranging from near perfect protection to complete destruction of the coated sample in a 20-month weathering period were observed.

Pigments are also used in conjunction with acrylic resins. The pigments are imbedded in the resin and applied to the canvas as a paint. Fabrics coated with such acrylic paints are reported to show improved weathering resistance [324].

Antioxidants. As mentioned, most authorities agree that the degradation of cotton fibers by the sun is caused by an oxidative process. While little information is available on increasing the resistance of cotton to oxidation, information from other areas should prove useful in research on this subject. Much is known about oxidation and reduction in general, and many chemical compounds that inhibit oxidation under a variety of conditions are commercially available. Inhibitors, called antioxygens or antioxidants, act as negative catalysts; that is, they lower the reaction speed. Their effect is the same as if the oxygen had become almost inert in their presence. A variety of materials subject to oxidation including rubber and food are protected by the addition of small quantities of such chemicals.

Phenols constitute the largest and most important class of antioxidants. Practically any phenolic substance or naphthol, with two or more hydroxyl groups ortho or para to one another, is likely to show some antioxidant properties. However, activity varies widely with the nature and position of substituent groups. Aminophenols and aromatic amines are also effective antioxidants.

The effectiveness of nonoxidative or reducing type finishes applied to cotton fabrics has not been thoroughly explored. Cotton duck has been treated with phenolic derivatives such as hydroquinone, pyrogallol, and α-naphthol alone and in combination with copper naphthenate [46]. After exposure to outside weathering, the fabrics finished with the pyrogallol-copper naphthenate yielded the best results. The mechanism of action of pryogallol was not studied. There are several possibilities based on the fact that pyrogallol is a strong reducing agent and would therefore be subject to changes after exposure [46]. A reaction may occur between the copper compound and the pyrogallol, making the former less available for catalytic activity. A second possibility is the bonding of the pyrogallol to the cellulose molecule in such a way as to block those groups which are the point of attack in the copper-catalyzed deterioration.

Ultraviolet light absorbers. Depending on the type of bonds present in their chemical structure, certain compounds which are colorless and absorb little or no light in the visible region may absorb radiation in the invisible spectral regions. Molecules that include the benzene ring in their structure, such as benzene, toluene, xylene and the like, show distinctive absorption patterns in the ultraviolet region. Derivatives of this type, commonly known as ultraviolet light absorbers, have been used in "suntan" oils and creams for over a decade and are now finding numerous industrial uses. They are included in plastics to prevent light degradation of polymer molecules, in methacrylate airplane canopies to protect the crew, in plasticized vinyl chlorides and styrene polymers, and in auto waxes and varnishes [131].

To be effective, an ultraviolet absorber must first absorb efficiently throughout the near ultraviolet region of the spectrum. Second, the absorber must be stable to ultraviolet light. Third, it must dissipate the absorbed energy in such a manner as to cause no degradation or color in the medium to be protected. Perhaps one reason why light absorbers are not as common as antioxidants or heat stabilizers is that most of them are not inherently light stable. Poor stability of an absorber may not be a handicap in a suntan lotion, but it rules out its application in protective coatings and plastics.

The substituted benzophenones are very effective agents for absorbing ultraviolet light, and of the organic compounds that have been studied for use as ultraviolet absorbers so far, the derivatives of 2-hydroxybenzophenone are the most stable and efficient [131]. Their stability and strong absorption characteristics are attributed to a conjugate chelation between the orthohyrdoxy and carbonyl groups [131].

The application of these substances to textiles has been considered in recent investigations [77, 131]. Simple and economical methods of utilizing them to improve the light resistance of fabrics are not available. None of the absorbers evaluated so far are substantive to cotton, although some of them can be dyed into wool and nylon [77]. The derivatives used, however, impart a yellow cast to the synthetic fiber, and this limits their usefulness on light-colored synthetic fabrics.

Another approach is to incorporate the ultraviolet absorber into a textile resin and apply it to the fabric [77]. However, the applied coating must be of a certain minimum thickness if the absorber incorporated in the resin is to be effective. In most instances, the amount of resin required to give the necessary thickness would greatly affect the hand of the fabric.

Chemical modification. As a class, vat colors head the list for all-round colorfastness on cotton and are therefore widely used. As previously discussed, some of these dyes make cotton more resistant to sunlight degradation; others (numerous yellows, oranges, reds, and browns) accelerate photochemical attack [19, 26, 68, 101, 124, 197].

The previously described acetylation process improves cotton's resistance to microorganisms but does not impart resistance to sunlight. Cotton can be made unusually resistant to weather by first dyeing it with certain light-stable vat dyes and following this with partial acetylation [40]. Data obtained on a number of individual vat-dyed and vat-dyed acetylated cotton materials that were exposed to outdoor weathering show that the service life of the acetylated dyed fabrics is more than double that of either the vat-dyed fabric or the acetylated fabric alone. Several vat dyes were tested, but only certain ones exhibited this synergistic effect. However, even those dyes which are recognized as promoting deterioration of cotton textiles under ordinary conditions of sunlight exposure were rendered less active by acetylation. That is, the acetylated dyed cotton retained appreciably more strength than the corresponding unacetylated dyed material.

Attempts to relate the degree of protection with chemical structure, color, and other properties of the dye were not successful. On the other hand, resistance to attack does seem to correlate with the lightfastness of the dye, since exposed samples which show the greatest color loss also exhibit the greatest loss in strength. Cottons dyed with basic, direct, sulfur, and naphthol dyes were acetylated, but the results were not as promising.

Protection from Atmospheric Acids

Several treatments for cotton fabrics offer some protection against corrosive substances in the air [79, 156, 169, 285].

Laboratory studies have shown that acetylated and cyanoethylated cottons are more resistant to the action of mineral and organic acids than ordinary cotton [79, 169, 285]. The protective effect is attributed to a blocking of the hydrolysis of the glucosidic linkages.

In applying chlorine- or halogen-containing elastomers or plastomers to fabrics susceptible to damage by chlorine or hydrogen chloride, it is customary to add a stabilizer or acid acceptor to neutralize or prevent acidity. For example, the so-called "FWWMR" or "fire-, water-, weather-, and mildew-resistant" finish for cotton duck contains calcium carbonate to neutralize acids resulting from the breakdown of the vehicle, chlorinated paraffin, by light or heat [156]. The presence of this alkaline compound would also tend to neutralize airborne acids which might come in contact with the fabric while in use.

Weather-Resistance Treatments

Progress has been made in improving cotton's resistance to the combined effects of weather [40, 46, 156, 324, 335]. One of the most successful all-purpose weatherproofing treatments is the aforementioned FWWMR finish, which consists of chlorinated paraffin, antimony oxide, calcium carbonate, inorganic pigments, and fungicides [156]. The destructive wave lengths of the sun are effectively screened out by the pigment combination of iron oxide, antimony oxide, lamp black, and calcium carbonate. Mildew and rot protection are afforded the fabric by the coating and fungicidal ingredients. Other pigment systems have been found to protect cotton equally as well as those mentioned above. The chlorinated paraffin acts as the vehicle for the pigments and also as a source of halogen, which in combination with the antimony salt produces fire resistance. This treatment was used widely during World War II for imparting weather and fire resistance to cotton duck, but it adds more weight than is commonly desired [40].

The vat-dyed acetylated cottons [40] and pigments applied in conjunction with various resins, stabilizers, and fungicides to cotton duck [64, 65, 324] offer improved resistance to both sunlight and microorganisms. Only the latter, however, is used commercially.

Most of the all-purpose weatherproofing treatments including the FWWMR and the vinyl and other synthetic resin coatings impart water resistance and would protect against degradation by alternate wetting and drying as well as the other weathering factors. Water-resistant or water-repellent properties may also be imparted to cotton by numerous other methods. These vary from strictly physical processes involving the construction of the fabric, or coating of the fibers with a hydrophobic material, to methods based on chemical modification of the fiber. Only a relative few of these, however, are suitable for outdoor fabrics. The physical processes are widely used because of their comparatively low cost. Coating treatments are usually carried out by the application of wax emulsions or other hydrophobic substances to the fabric in a "one-bath" process.

Weather-resistant finishes which coat the fibers would tend to increase the flat abrasion resistance of fabrics. These treatments, on the other hand, would tend to increase damage from flex abrasion because of increased friction between fibers and yarns.

Test Methods

The optimum test method is one which, in a short period of time, would provide data correlating directly with the performance of the fabric in actual service. This has proved to be an extremely difficult goal because of the lack of a standard weathering pattern. Because weathering is a complex interaction of several variables, its effects on cotton textiles vary with the time of the year and the location and are never precisely predictable or reproducible.

Numerous methods [1, 43, 81, 84, 122, 300, 343] have been proposed for evaluating the weather resistance of cotton textiles. In some of them the fabric is exposed out-of-doors to all the factors involved in weathering, while in others it is subjected separately to one or more of the individual factors in the laboratory. At present, field exposure under conditions of expected use is the most widely accepted method for evaluating the effectiveness of treatments. This method, however, poses the difficulty of finding a measurable property which will give an indication of relative value. The best indicator, and the one which correlates with actual use, is the length of serviceability. The reasons for which a fabric becomes unserviceable are many and varied (tearing, abrasion, color loss, etc.) and their relative importance depends on the use to which the article is to be put. Laboratory testing methods which depend upon the evaluation of the effect of individual factors, such as light or microorganisms, cannot be counted on to provide dependable information. Studies have indicated that no constant relationship exists between the results of such tests and field exposure tests [124]. It is therefore necessary, in setting up a testing program, to select the important properties that should be evaluated and to decide which of the many different test

methods available are most appropriate for the purpose to be served. This requires an understanding of the significance and limitations of each method and test results to be expected.

Field Exposure

The most common method for testing the resistance of cotton textiles to weathering is by outdoor exposure. The most exacting tests of this type are service tests which seek to duplicate end use conditions as closely as possible. Fabrics are made into tarpaulins, tents, or other items and exposed to actual use conditions. Testing by outdoor service exposure, however, is expensive and time-consuming, since a large number of items must be exposed for long periods of time in order to obtain significant results. Consequently, this method is used only after preliminary screening by simpler procedures.

Industrial, private, and government research organizations maintain experimental stations in tropical or semitropical areas where the fabric samples are exposed to the weather, as shown in Figure 15. Swatches of fabric are mounted on racks or parallel bars on which the fabric is fully exposed to the sunlight. Control samples are mandatory in these investigations, as the final results depend on the actual weather conditions during the exposure period. Time and location play a large part in determining the results.

In outdoor exposure tests the fabric is vulnerable to attack not only from the rays of the sun but also from microorganisms, airborne acids, and other factors of weathering. The variability of these factors is, of course, a hindrance in determining accurately the cause of any deterioration which occurs. It is possible, however, to differentiate between the deterioration caused by microbial attack and that produced by sunlight or airborne acids [22, 46, 254]. This differentiation can be made by virtue of the fact that microbiological attack reduces fabric strength but does not affect the fluidity of the residual cellulose in solution, whereas the action of sunlight and airborne acids both produce an increase in fluidity. Figure 16 shows a typical curve based on several thousand measurements on cotton fabrics exposed in shaded jungles and in sunny areas in the tropics. The fabrics exposed in the shade where microbial attack was predominant show no change in fluidity, in striking contrast to the increases obtained with those exposed to the sun. The increased fluidity is indicative of the stepwise scission of the cellulose molecule into smaller frag-

Fig. 15. Swatches of fabric mounted on racks fully exposed to the weather.

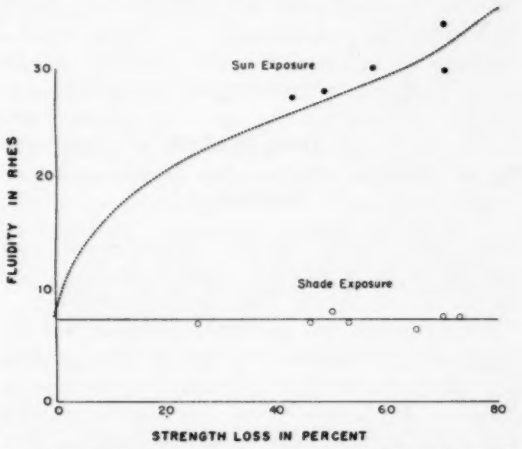

Fig. 16. Relation of cuprammonium fluidity and tensile strength of cotton cloth exposed in Panama.

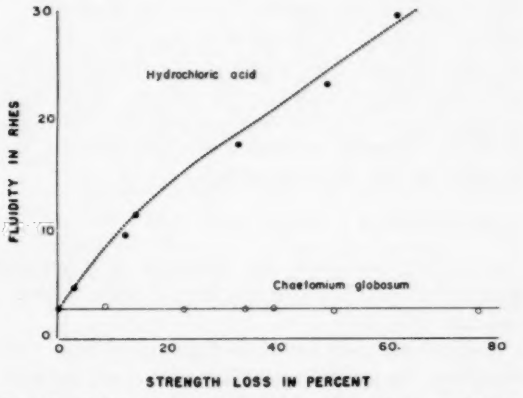

Fig. 17. Effect of chemical and biological agents on fluidity and tensile strength of cotton fabrics.

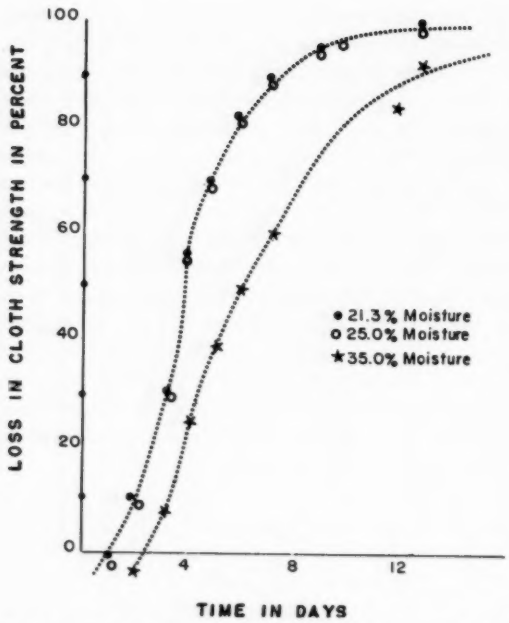

Fig. 18. The effect of soil moisture on the rate of fabric breakdown.

ments. As shown in Figure 17, similar results were obtained in the laboratory, using hydrochloric acid and the microorganism *Chaetomium globosum.*

The methylene blue absorption technique and the copper number or reduction test are also valuable aids which may be used in determining the type or extent of degradation [245]. A positive reaction with either method indicates that cellulose has been oxidized. On oxidation, the hydroxyl groups on the cellulose molecule are first converted into aldehydic groups which on further oxidation are changed into carboxyl groups. Absorption of methylene blue by cellulose indicates the presence of carboxyl groups, while the copper reduction procedure, which is a measure of the power of cellulose to reduce Fehling's solution to metallic copper, is used to determine the presence of free aldehyde groups.

Mildew and Rot

In testing materials for resistance to microbial degradation in the laboratory, the following methods are commonly used.

Soil burial. Soil burial is the most drastic and, therefore, for quick evaluation, the most popular testing method [30, 43, 219]. This procedure is often used as a substitute for outdoor exposure. One week of soil burial is estimated to be equivalent to about one year of outdoor exposure, thus making it possible to screen large numbers of potential preventive agents in a short period of time [300]. The test consists of burying (vertically, horizontally, or at an angle) 1-in. raveled strips of fabric in soil containing a variety of organisms. A good greenhouse or potting soil is adequate. The water content and temperature of the soil are quite important. This is illustrated in Figure 18, which shows the effect of soil moisture on the rate of fabric breakdown. Soil burial tests are usually carried out in rooms or cabinets with the temperature controlled within a range of 85°–90° F. The loss in breaking strength of the fabric, after burial for periods of from one to nine weeks, serves as an index of resistance. As in other biological tests, untreated material of the same type as the treated test sample is tested at the same time to show that organisms responsible for deterioration are present and active.

The value of the soil burial test lies in evaluating the performance of fabrics to be used in contact with the soil. One of the difficulties involved with its use is the high degree of variability of results from different soils. This is caused by the fact that different soils contain different types and numbers of organisms. However, it has been shown that, although the absolute values for resistance to deterioration of a series of samples often differ from one soil to the next, the relative ranking of various samples is frequently consistent in different soils.

Soil suspension. The soil suspension method [1, 118, 287], although less severe, is related to and at times is used as a substitute for the soil burial test. The fabric sample is immersed in a water suspension of soil containing a mixture of unknown organisms and incubated for a specified period of time. Reproducible results are difficult to obtain, but the soil suspension method is a rapid, convenient test for determining the resistance of treated fabrics to mildew and for ranking them by order of effectiveness.

Pure culture technique. The pure culture technique is a controlled laboratory test [1, 137, 219, 300]. A sterilized sample of fabric is placed in a culture vessel, such as a culture bottle, Petri dish, or flask containing a mineral or organic nutrient. A single species or a mixture of known microorganisms is then applied. Specimens are incubated at a temperature of 85° F. and a relative humidity of 95% for specified periods of time. Results of the

test are usually reported in terms of breaking strength losses and amount of visible growth.

The proper selection of organisms is of major importance in this test. In detailed research and development studies the question is frequently raised as to how many different species should be used. Organisms differ with respect to their rate of cellulose breakdown, geographical distribution, resistance to fungicides, and reaction to changing environmental conditions. The selection of organisms depends, of course, on the objectives of the study. The greatest advantage of a mixed culture is the simultaneous exposure of the treated fabric to a number of organisms with different tolerances to fungicides and physiological requirements. This would presumably be a more severe test than exposure to a single species. On the other hand, it has been observed in field-exposure tests that exposed cotton fabrics are usually attacked by one predominant species rather than by a mixture. The conclusion would be then that the use of a single species in pure-culture tests would be more representative of field conditions than a laboratory mixture.

Tropical test chamber. As an intermediate between actual field exposure and controlled laboratory tests, a tropical test chamber has been developed [81]. These chambers are enlarged incubators with the temperatures kept constant at about 85°–90° F. and the relative humidity at about 95%. Some are the size of a large room, and the temperature and humidity are varied to correspond to the fluctuating day and night temperatures in the tropics. Biological flora are enriched by strewing leaves and soil on the floor. The room may also be inoculated with known cellulolytic organisms, thus superimposing a known upon an unknown microbial population. Noncellulolytic organisms are sometimes included to insure the presence of a rapid surface-growing species on the noncellulosic components of the finished fabric. The samples to be tested are exposed either in contact with the soil or are suspended in the air above the soil. Different lengths of exposure time, from several weeks to a year, are used, and periodic checks on the strength and mildew coverage are made.

Tropical test chambers are expensive to operate. They are used primarily as a pilot-plant testing area for items or material components.

Mycelial mat method. The mycelial mat method [1] is intermediate in severity between the pure culture and soil burial methods. It consists of laying the fabric samples, which have been inoculated with an organism, on vigorously growing mats of the same organism in culture bottles. The bottles are then incubated for specified periods of time. Evaluation of the sample's resistance to the microorganism is usually by measure of the loss in strength. With this technique, only one of the influences, that of mycelial growth, is measured. In natural exposure, spores frequently germinate and grow on debris on the fabric surface. The mycelial mat method approaches these conditions more closely than the methods calling for direct spore inoculation.

Manometric technique. In the previously described methods, loss in breaking strength is the commonly used procedure to determine quantitatively the amount of attack of cellulolytic organisms. Loss in weight of the fabric sample is also occasionally employed. A third indication of the degree of microbial action is the amount of carbon dioxide liberated, or oxygen consumed, during the attack of the organism on the textile material [214]. This is a rapid manometric technique in which the criterion of mildew susceptibility is not based on changes in the fabric, but rather on the total oxygen absorbed by the microorganism during growth. The more resistant the fabric, the less growth it supports and the less the volume of oxygen consumed by the organism. The time required for a test varies from one to two days.

Sunlight

Fabrics are tested for resistance to photochemical deterioration by exposing them to the sun or to an artificial source of light which has characteristics similar to those of sunlight. In sun exposure tests, the fabric is placed in a well ventilated cabinet and protected from rain and dust by a glass cover [122]. Since ordinary window glass acts as a filter to screen out ultraviolet radiations below 3400 Å, special glass, with transmission characteristics similar to the spectrum of sunlight, is used to cover the exposure cabinets.

The main advantage of using artificial light sources is that tests are not restricted to certain hours of daylight or fair weather, but can be run continuously 24 hours a day until the test is completed. Degradation is measured either by loss in breaking strength or by increase in fluidity. As in other types of testing, loss in breaking strength is more frequently used because of the ease of measurement.

Of the available light sources, the high-intensity carbon arc with appropriate filters appears to give

the most reproducible results [15, 84]. With the use of a special glass filter, its spectral characteristics closely approach those of natural sunlight. The spectral range of a Corex-enclosed carbon arc is approximately 2900–40,000 Å, as compared to a range of approximately 2900–30,000 Å for sunlight at sea level. It has been shown, however, that this light source is of little use for predicting the durability of chemically finished cottons in outdoor service [92, 124].

The carbon arc is used as the light source in the Weatherometer, which was developed for accelerated testing or screening purposes. In this apparatus, the fabric sample may be exposed to synthetic sunlight, mild or vigorous rain (water spray), and temperature changes. The Fadeometer, which is used to determine the resistance of dyes to fading, also employs the carbon arc as its light source.

A second artificial light source used to study the effects of the sun's rays on fabrics is the mercury vapor lamp. Its spectral range is 1,800–14,000 Å, with an especially strong distribution in the ultraviolet range. One of the disadvantages of this lamp is the production of ozone, which may cause inaccurate results [15, 106, 343]. The radiation from the mercury vapor lamp is not constant, as it tends to change in quality and intensity with continued use [15].

At present, methods specifically designed for the testing of a fabric's weathering resistance to atmospheric acids and abradants are not available. The Weatherometers can be used for alternate wetting and drying tests on fabrics. As previously indicated, this apparatus is recommended primarily for screening purposes.

Opportunities for Future Research

The following suggestions are offered in the hope that they will stimulate thinking and generate new ideas for worth-while research.

Mechanism of Action

Much is still to be learned about the actual mechanisms involved in the outdoor weathering of cotton. The lack of information has necessitated the development of preventive methods by a trial-and-error and comparison program. Because of the complex interaction of the factors involved in the weathering process, research must first be directed toward separating and studying each of them separately. Only after the individual role of each agency is better understood can useful investigations be conducted on their interaction in the deterioration of cotton.

Mildew and rot. A great deal of research has already been conducted on one of the major degradative mechanisms, the microbiological process, and considerable progress has been made. At the present time, however, there is an unclear picture not only of the gross attack of the microbes upon the fabric but also of the mechanisms involved in the microbial breakdown of cotton cellulose. Various opinions are found in the literature as to whether the organisms penetrate the lumen and degrade the fibers from inside out or whether the attack starts from the outside and proceeds inward. There is also some evidence that the secondary wall of the fiber may be directly penetrated by the fungal hyphae. Knowledge of the manner in which microorganisms attack cotton fibers and bring about reduction in tensile strength would be very useful for an understanding of the basic requirements for satisfactory methods to prevent microbiological attack. A technique for utilizing the electron microscope, with its tremendous magnification and resolving power, might make direct observation of the sites of attack possible and thereby contribute to a solution of the problem. It would also be advisable to determine whether or not the hyphal penetration of the fiber is randomized or whether minute differences at various points along the fiber surface induce selective penetration at particular points. The fiber, it appears, is liable to initial attack at several points. These are: broken ends of hairs and deep cracks reaching the lumen, abrasion and shallow cracks, and normal fiber surface. Studies should be carried out to determine the exact route or routes taken by the organism.

Little is known about the chain of chemical conversions undergone by the cellulose molecule during microbial attack. Knowledge of these reactions would afford an important background for devising mildew- and rot-resistant finishes. This would be especially true if the initial molecular transformations were known. The mechanisms of many biological reactions have been worked out by the isolation and identification of intermediate chemical products. In the case of the microbiological degradation of cellulose, this approach has not met with much success because of the rapid degradation of the cellulose molecule into very simple compounds. Investigators have also been hampered by the fact that they are unable to separate the enzymes responsible for the degradation into pure fractions. Consequently,

nearly all of the work has been carried out with organisms, and the results of such experiments are confused with the effects of secondary metabolic processes. If separation of these enzymes could be effected, the researcher's task of isolating and identifying the metabolic products would be made easier.

It is possible that there is more than one metabolic pathway for different organisms. The increasing evidence of the complexity of these mechanisms requires that better methods be developed for the isolation of the enzymes. Differences in absorptive properties, in electrical charge, and in solubility may all need to be employed to effect the desired separation [257]. Once the components have been isolated, several other avenues of attack on the problem will be opened. The use of radioactive tracers or mass isotopes would enable the investigator to follow the various transformations through the use of the Geiger counter and mass spectrograph.

Sunlight. The exact mechanism by which the photochemical degradation of cotton takes place is still obscure. The effects of light, moisture, and oxygen (or ozone) appear to be inter-related, and the reactions which occur are thought to be oxidative in nature. A better understanding of the action of the sun's rays on cellulose would be of considerable aid in developing successful treatments to inhibit or prevent photochemical action. Chemical studies directed at investigating the degradative reactions that occur should be initiated. One approach would be an attempt to identify the degraded products, which would give some insight into what reactions are taking place. The infrared spectrophotometer has been used successfully for identification purposes in recent years and might prove to be of value in this instance.

Recent investigations [86, 134] have shown that mercerized cotton is more resistant to sunlight and to weathering than unmercerized cotton. This, of course, suggests an improved base fabric for further finishing of cotton textiles which are exposed to sunlight and weather. So far, no specific explanation has been given for the better weathering qualities of the mercerized fabric, which may have one-third to one-fourth longer service life than an untreated cotton fabric [134, 155]. At first glance, a simple reason for the improved light resistance is that mercerized cottons possess a higher degree of luster and therefore reflect more incident light than an unmercerized sample. Spectrophotometric measurements show, however, that a mercerized cloth has less reflectance and greater transmittance than an unmercerized sample [134, 177]. Further work on the effects of mercerization and other purification finishes on the light resistance of cotton fabrics is suggested, since such investigations should contribute to our understanding of photochemical degradation and the development of better preventive methods.

Swelling in mercerization changes the crystalline–amorphous ratio in cotton, opening the structure and bringing it closer to that of rayon, in which there is less internal interference with the passage of light. This is evidenced by greater fiber transparency. Efforts should be made to find out how much of the light entering the mercerized fiber passes completely through, how much is diffused by what remains of the lumen, and how much is scattered by the fibrillar structure. Answers to these questions would be of considerable aid in determining the mechanism of mercerized cotton's improved resistance to sunlight and would also provide additional information on photochemical degradation and methods which can be used to combat it.

Other factors. The importance of the secondary degradative mechanisms and their relation to the over-all picture of weathering has not been fully evaluated. Degradation by corrosive acids is a factor in highly industrialized areas, but just how much of a factor is not known. In the action of sunlight on textiles, conditions of exposure as well as the quality and intensity of radiation accelerate or decelerate photochemical action. Although oxygen is thought to have the greatest influence on photochemical activity, moisture, temperature, and air currents also modify the rate of degradation, and it is important to know the extent to which they do this. Further studies of these mechanisms, their relative importance in the over-all picture, and their interrelationship with the other factors of weathering are suggested.

Preventive Methods

Additive finishes. At present, additive finishes or coatings are the most common weather-resistant treatments for cotton fabrics, but only a relatively few can be described as durable and acceptable for outdoor use. In addition, the effective weatherproofing and light-screening additive finishes so far produced have usually resulted in stiff, boardy products with high add-on weight and without many of the properties of a textile fabric. Studies should be continued toward finding durable treatments which are

capable of protecting cotton fabrics against weathering with fewer adverse effects on weight and hand.

Additive treatments offer many possibilities for the improvement of fabric weathering properties. The durability and protective properties of such finishes could be considerably enhanced by improving the individual components of the formulation. Even when applied in conjunction with other materials, the most effective fungicides are often removed. Many of the organic inhibitors often break down on outdoor exposure to yield water-soluble products and, in addition, have a tendency to accelerate photochemical degradation of the fabric. Research efforts should be continued toward the development of durable fungicides which do not have undesirable side effects on cotton fabrics when exposed outdoors.

The use of a single fungicide often has some fundamental shortcomings. As previously discussed, various species of microorganisms may become or are immune to certain inhibitors. Limited laboratory and field investigations [33, 108, 335] have shown that the effectiveness of some individual inhibitors may be increased by using them in combination with one or more different fungicides. (In such mixtures care must be taken as to the chemical compatibility of the components.) Despite the promising results obtained with some fungicidal combinations, only a few are used commercially. Additional studies should be made to evaluate the relative performance and advantages of various combinations of inhibitors as compared to individual fungicides.

Recent investigations [64, 65] have shown that inorganic and organic pigments have widely divergent effects on the weather resistance of canvas. The compounds studied, while representative, are only a comparative few among the large number of pigments available to the coater. Extensive studies covering the individual pigments should be made to establish which compounds offer the best protective results. Little information as to how these pigments afford protection is available. A research project resulting in an answer to this question would furnish fundamental information regarding the action of the sun's rays on the fabric and point the way to a selection of more resistant treatments.

The addition of an antioxidant, such as hydroquinone or pyrogallol, to cotton fabrics should tend to prevent the oxidative degradation which occurs when cotton is exposed to the rays of the sun. The extremely limited amount of work in this area has shown some promise, and it would seem that additional organized research should be attempted. Much information on the type of compounds required has been developed by research workers in other fields, such as the rubber industry, where oxidation is a problem which has been met and conquered. Additional studies should be made to evaluate the protective effect of these antioxidants and their application to cotton fabrics as part of a durable finish, dye, or dyelike material.

Benzophenone derivatives have been found to be inherently light stable and very effective absorbing agents for ultraviolet light. None of the absorbers of this type investigated thus far are substantive to cotton. Presumably, they could be made a part of a durable finish or coating. In most instances, however, the weight of the resin to give the required thickness for an effective screen would greatly affect the hand of the fabric. If the absorber were located in the cotton fiber rather than in a thin surface film, it should be more efficient in protecting the fabric and also the dyes which are within the fiber [131]. Just how this might be accomplished with cotton fibers has not been determined. However, the technology of applying absorbers to textiles has only started to be developed, and studies should be directed at finding simple and economical methods of utilizing them to improve the weatherability of cotton textiles.

Chemical modification. Practically all derivatives of cotton cellulose exhibit a higher resistance to microbial action than cellulose itself. So far, however, few treatments are available which will reduce photochemical degradation and also give a high degree of protection against microbiological attack. Along these lines, chemical modification offers several interesting approaches. Considerable information is now available on the relationship between the structure of organic groups and their ability to absorb specific wavelengths. Cotton fabrics coated with various sulfonylamino derivatives have been found to withstand sunlight exposure much better than untreated cloths [315]. Compounds similar in structure to these light-screening agents have been reacted with cotton, and the modified fabrics were found to be resistant to microbiological degradation in soil burial tests [329]. Such reactions require further study. Other light-screening substituents should also be evaluated in that it should be possible to attach a group of this type to cotton fabrics and obtain simultaneous protection against microorganisms and sunlight.

While little has been done to give cotton durable resistance to oxidation, information from other fields might prove useful in research on this subject. Much is known about oxidation and reduction in general, and many materials are known that inhibit oxidation under some conditions. Reeves [259] has shown that it is possible to attach an antioxidant chemically to the cellulose chain. Other antioxidants should be investigated as to their reactivity with cotton and their effects on the weathering characteristics of cotton fabrics.

Accelerated Weathering Tests

At present, the field exposure test under conditions of expected use is, by far, the most reliable method for the evaluation of the effectiveness of treatments. There is need for a dependable accelerated method of testing the serviceability of textile products designed for outdoor use. In screening a group of experimental weather-resistant finishes, it would be of obvious advantage to have available a rapid method for testing that would dispense with time-consuming outdoor exposure, which usually requires from 12 to 36 months.

Accelerated tests have been developed for testing the resistance of fabrics to microorganisms and sunlight. To be of value, the results of these methods must have some degree of practical correlation with those of natural weathering. As yet, however, none of these artificial tests has been found reliable in predicting the behavior of finished cottons in outdoor service conditions. Efforts should be continued toward finding fast, reproducible laboratory methods that correlate with service.

Acknowledgment

The authors wish to acknowledge the important contributions made by the staff members of the National Cotton Council of America for advice and help in preparing this report and the considerable technical assistance provided by authorities in this field. It should not be inferred that the technical opinions presented necessarily represent the views of these authorities, among whom the following have been especially helpful: R. G. H. Siu, Office of the Quartermaster General, Washington, D. C.; Stephen Kennedy, Allen McQuade, and Elwyn T. Reese, Quartermaster Corps, Natick, Massachusetts; Lawrence L. Heffner, School of Textiles, North Carolina State College (USDA), Raleigh, North Carolina; William Appel, National Bureau of Standards, Washington, D. C.; Wilson Reeves, A. S. Cooper, John D. Guthrie, and W. Norbert Berard, Southern Utilization Research and Development Division, U. S. Dept. of Agriculture, New Orleans, Louisiana; Edward Buras and Herman Bogaty, Harris Research Laboratories, Washington, D. C.; Carl J. Wessel, National Academy of Sciences, Washington, D. C.; C. H. Bayley, National Research Council, Ottawa, Canada; and Paul B. Marsh, Agricultural Research Service, U. S. Dept. of Agriculture, Beltsville, Maryland.

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Manuscript received September 8, 1959.

Shrinkproofing of Wool with Polyglycine from the Polymerization of Thiazolid-2:5-Dione

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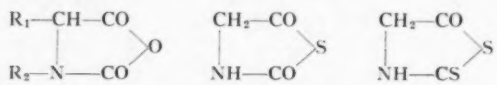
Abstract

Shrinkproofing of wool with thiazolid-2:5-dione is not possible from aqueous solution but can be obtained from a range of organic solvents of low water affinity at temperatures $> 40°$. The abrasion resistance of treated fabric is about 1.5–2 times that of untreated fabric but cost of treatment would be prohibitive in practice. Since the polymerization of dione is initiated by water in the wool, the polyglycine (number average degree of polymerization about 18) cannot be attached by covalent bonds but by intermolecular hydrogen bonds. Descaling shows that most of the polyglycine is located in the scales; a thin surface layer can be seen under the electron microscope. This surface layer reduces the directional frictional effect and produces shrinkproofing with a weight increase of the fiber of only 1%. It is most unlikely that spot welding of fibers with polyglycine is a contributing factor towards shrinkproofing.

Introduction

Shrinkproofing of wool with polyglycine by polymerization of anhydrocarboxyglycine (Number 1 below, where $R_1 = R_2 = H$) was first investigated by Baldwin, Barr, and Speakman [4, 5]. Successful treatments were not possible in aqueous solution, due to initiation of polymerization by water [8] with subsequent precipitation of polyglycine in the solution, but satisfactory results were obtained from ethyl acetate solution. The main disadvantages of this process are the use of an organic solvent and the instability of the monomer in the presence of moisture at room temperature. In an attempt to find a more stable monomer, Alexander, Bailey, and Carter [2] examined a range of N-carboxy acid anhydrides of the general formula Number 1 (where R_1 and R_2 are hydrogen, alkyl, or phenyl groups) as well as thiazolid-2:5-dione (Number 2) and 2-thiothiazolid-5-one (Number 3). They found the optimum conditions for shrinkproofing with anhydrocarboxyglycine



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from diethyl carbonate solution and then tried the other monomers under essentially these conditions, when little or no shrinkproofing was obtained. They therefore conclude that the other monomers are of no use, but this is not justified, since the monomers differ in reactivity; hence the optimum conditions of application of each one must be determined by a separate series of experiments. Because of its relative stability towards water as compared with anhydrocarboxyglycine [2, 3], thiazolid-2:5-dione (dione) was investigated; we obtained the optimum conditions for its application to the shrinkproofing of wool.

A small amount of water was found to be essential for the shrinkproofing of fabric with anhydrocarboxyglycine in an organic solvent [2, 5]. Alexander et al. [2] thought that the water present initiated polymerization of anhydrocarboxyglycine to produce polyglycine which would not be covalently attached to the wool. However, Speakman and coworkers [5] proposed that the ϵ-amino group of lysine initiated polymerization, in which case the polyglycine produced would be covalently attached to the wool fiber. These opposite conclusions were based on the results of experiments to see whether deaminated wool could be shrinkproofed and also whether the polyglycine could be dissolved by treatment of the shrinkproofed wool sample with concentrated aq. lithium bromide solution. End-group methods have been used to decide the question in our case and to obtain the degree of polymerization of the polyglycine on the wool. The location of the polyglycine on the fiber has also been investigated by optical and electron microscopy and by the descaling

technique [12, 13]. A subsequent paper [14] will deal with the shrinkproofing of wool by polyglycine produced by the polymerization of anhydrocarboxyglycine.

Experimental

Materials

Thiazolid-2: 5-dione (dione). About 150-g. quantities of this material were prepared by the method of Aubert, Jeffreys, and Knott [3]. The crude products were recrystallized from A. R. chloroform and dried in air; the melting point was 108–110°. The purity of the various batches of material was always checked by one or both of two methods. The first method involved the rapid titration of a solution of the dione in methanol or chloroform with 0.15 *N* CH_3ONa to the end point with either thymol blue or phenolphthalein [6, 9]. Calculated purity was 94–98%. The second method was to measure the amount of COS evolved in the reaction between 0.5 g. dione and 5 ml. water in a constant volume apparatus fitted with a manometer [7]. The reaction of COS with water is slow enough to be neglected [29]. The purity calculated on the assumption of zero decomposition of COS was 90–93%. Further purification by dissolving in cold ethanol, pouring into petroleum ether (Shell, X222 solvent) and cooling to 0° produced material which was no more effective in shrinkproofing wool fabric from white spirit than the 90–93% pure material. This justified the use of the latter in all experiments unless otherwise stated.

Polyglycine. Dione was polymerized in distilled water for 64 hr. at room temperature and the polyglycine filtered off, washed with water, and dried.

Wool fabric. A plain weave worsted fabric made from Merino 64's wool was used with the following construction: warp yarn 2/30's, weft yarn 2/30's, 30 ends/in., 30 picks/in.

Wool top. Lincoln 36's top was extracted in a Soxhlet apparatus with petroleum ether for 4 hr., dried, and extracted with four changes of water at 50°, each of 15 min. duration. The top was centrifuged and conditioned at 65% RH and 20°.

Chemical Methods

Treatment of fabric and top with dione. Fabric squares (4 g.) were treated with dione in solution with intermittent stirring which was effective in preventing uneven treatment. A 22-g. sample of top was treated with 2 g. dione in 200 ml. white spirit at 80° for 20 min. The top was washed twice in acetone to remove unreacted dione, centrifuged, and conditioned at 65% RH and 20°. A shrinkage test on part of it gave a length shrinkage of 9% compared with 42% for an untreated sample.

Glycine analyses of whole fiber and scale-rich material. About 0.4-mg. samples were analyzed by the dinitrophenylation method [13]. It was necessary to determine all the amino acids estimated in this reference in order to check that an approximately 100% yield of amino acids was obtained.

Determination of N-terminal end groups and ε-amino lysine groups. Samples of untreated and dione-treated top were exhaustively dinitrophenylated and washed by the method of Fritze and Zahn [15]. Polyglycine was also dinitrophenylated in aqueous $NaHCO_3$ solution at 60° for 5 hr. with an extra addition of 1-fluoro-2:4-dinitrobenzene (FDNB) after 2½ hr. had elapsed, then washed as prescribed for wool [15].

Because of the considerable extent of decomposition of DNP-glycine during hydrolysis of DNP-wool in 6 *N* HCl [23], an attempt was made to use anhydrous mixtures of perchloric acid with glacial acetic acid or with formic acid and acetic anhydride [16]. However, these mixtures were found to give incomplete hydrolysis after heating at 100°, as shown by the appearance of numerous unidentified yellow spots on the two-dimensional chromatogram, which were presumed to be DNP-peptides.[1] Hydrolysis of DNP-wool in twice distilled 6 *N* HCl under vacuum in a sealed tube was then investigated as follows.

A sample (0.1–0.2 g.) of DNP-wool at 65% RH and 20° was placed in a scrupulously clean Pyrex test tube, 4 ml. of 6 *N* HCl added, and the tube sealed under vacuum. After it was heated at 105° for the required time it was opened and the solution filtered and diluted to about 20 ml. with distilled water. It was extracted with 5 5-ml. portions of ether followed by 4 10-ml. portions of n-butanol. The ether layer was divided into two portions, each of which was applied at the origin of a two-dimensional paper chromatogram. The paper was run, the spots identified, cut out, and their intensity measured as previously described [13]. The n-butanol solution was evaporated to dryness and the residue dissolved in

[1] It is necessary to mix formic acid, acetic anhydride, and perchloric acid very carefully to prevent the occurrence of a very violent reaction.

acetone and made up to 25 ml. Aliquots (0.125–0.25 ml.) were applied to the paper together with an ε-DNP-lysine control spot and run in one dimension using the phosphate solvent [13]. The spot due to ε-DNP-lysine was cut out and the amount of material present determined in the usual way [13]. A sample of DNP-polyglycine (0.01 g.) was likewise hydrolyzed and the DNP-glycine separated and determined.

Determination of C-terminal end groups. The hydrazinolysis method [11] was used. The C-terminal amino acids were separated by two-dimensional paper chromatography using the toluene-phosphate buffer system [11] and also a second system based on t-pentanol-phosphate buffer [13].

Physical Measurements

Felting shrinkage. Fabric samples were relaxed in an aq. solution containing about 0.1% sodium sec.-alkyl sulfate (Teepol) and 2% $NaHCO_3$ for 30 min., then centrifuged; a square pattern of spots was put on the fabric [18]. The samples were washed in water at 35–40° in a washing machine of the horizontal cylindrical rotating cage type with a constant load of 6-in. squares of linen (total weight 1000 g.) until an untreated control showed an area shrinkage of about 40%. The area shrinkage of the treated sample was calculated on the basis of a 40% area shrinkage of the control.

Samples of top about 25 cm. long were machine sewn perpendicular to their length at two points about 20 cm. apart. The samples were relaxed and centrifuged as described above and the distance between the two sewn lines measured accurately with each top under constant tension. The tops were placed in glass tubes, 30 cm. long and 4 cm. in diameter, which were stoppered at both ends and contained 200 ml. distilled water. These tubes fitted into an apparatus (the prototype of which was developed by Mr. J. Curtis, Division of Textile Physics, C.S.I.R.O., Ryde, N.S.W.), such that they could be rotated at constant speed in a vertical plane about their central point. After 900 revolutions the machine was stopped and the distance between the sewn lines measured again under constant tension. The length shrinkage was calculated on a percentage basis as compared with an untreated control.

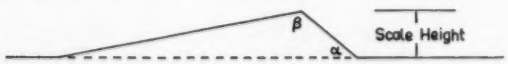

Fig. 1. Idealized scale profile of Lincoln 36's fibers.

TABLE I. Shrinkproofing with Dione in Various Organic Solvents*

Solvent	Solubility of water in dry solvent at 60°, %†	Area shrinkage, % (control = 40%)	
		Treatment from dry solvent	Treatment from water-saturated solvent
Carbon tetrachloride	0.025	0	0
White spirit‡	about 0.06	0	—
Chloroform (0.75% ethanol)	0.17	1	—
Benzene	0.26	1	—
Amyl acetate	1.2	1	2
Butyl acetate	1.8	28	9
n-Decanol	1.9	22	10
Ethyl acetate	5.3	32	—
n-Butanol	23.6	25	—
Methanol, ethanol, acetone and dioxane**	miscible	25 ± 2	—

* Fabric (4 g.) treated with 0.5 g. dione in 100 ml. solvent at 60° for 16 hr. with intermittent stirring.

† Solubilities in amyl acetate, butyl acetate, and n-decanol were measured volumetrically at 60°; the others were obtained from Seidell [27].

‡ Petroleum fraction, boiling range 150–205°.

** The solution after treatment was often milky due to precipitation of polyglycine.

Bursting strength and abrasion resistance. The bursting strength of fabric was measured on a Mullen type tester and the abrasion resistance on a Martindale tester using stainless steel mesh as the abrasive surface.

Frictional properties. The coefficients of friction of Lincoln 36's fibers were measured by the capstan method of Lipson and Howard [21]. Three measurements were made on each fiber at 20° and the fiber and keratin rod were exposed either to air at 65% RH, an aqueous solution, or white spirit.

Microscopic measurement of average scale shape. The experimental technique consisted in dyeing the ends of six Lincoln fibers different colors. Each fiber was examined at a magnification of 960× beginning at the junction of the dyed and undyed sections and working along the undyed section. The image of the fiber was projected onto paper and the outline marked carefully with a pencil. About 50 scale profiles were examined and the vertical height of each scale measured, together with the angles α and β shown in Figure 1. The six fibers were then mixed in a 10-g. sample of untreated Lincoln 36's

top and treated for 1 hr. at 80° in 100 ml. white spirit containing 1 g. dione. After being washed to remove loosely attached polyglycine, the partly dyed fibers were removed from the shrinkproofed top (length shrinkage 9%, control = 23%), and examined under the microscope over the same length as before. Unfortunately, it was not possible to measure exactly the same scale profiles as before, since there was no way of reproducing the original lateral orientation.

Results

Treatments in Aqueous Solutions

Experiments were made using 3.5–4 g. squares of fabric in 100 ml. buffer solution (0.05–0.2 *M*) or distilled water. The conditions of treatment were varied over the ranges pH 3–10, temperature 20–80°, and times up to 16 hr. As the pH was increased above 8 the degree of shrinkproofing progressively increased, due to the liberation of COS and its subsequent breakdown to alkaline sulfide which shrinkproofed the fabric. This conclusion was reached by replacing the dione with an equivalent amount of Na_2S when the same degree of shrinkproofing was achieved.[2] Below pH 8 only a slight amount of shrinkproofing was observed, accompanied by very slight increases of dry weight of the fabric after treatment. The solutions after treatment were often cloudy due to precipitation of polyglycine. Polymerization of the dione therefore occurs almost exclusively in the aqueous solution rather than on the fabric.

Treatments in Non-Aqueous Solutions

Effect of solvent. The results in Table I show that shrinkproofing with dione can be achieved in those solvents which have a sufficiently low affinity for water. Butyl acetate and n-decanol, which do not fall into this category, can be made suitable solvents for shrinkproofing with dione by saturation with water. The experiments reported in Table II allow a further differentiation between these solvents of low water affinity. It can be seen that, with the exception of benzene, the ease of shrinkproofing decreases as the solubility of water in the solvent increases. Since white spirit is both effective and cheap, most subsequent experiments were made with it as solvent.

TABLE II. Shrinkproofing with Dione as a Function of Solvent and Time of Treatment*

Solvent	Solubility of water in solvent at 60°, %	Solubility (wt./vol.) of dione in solvent at 60°, %†	Area shrinkage, % (control = 40%) after treatment for 0.5 hr.	1 hr.	2 hr.	5 hr.
$CHCl_3$ (sat. with water)	0.00	3.2	26	13	3	1
CCl_4	0.025	0.20	32	10	1	0
White spirit	about 0.06	0.05	35	13	1	0
Toluene	0.15	0.67	37	32	9	0
$CHCl_3$ (0.75% ethanol)	0.17	3.2	35	32	28	18
Benzene	0.26	0.60	35	29	3	0

* Fabric (4 g.) treated with 0.5 g. dione in 100 ml. solvent at 60° with intermittent stirring.

† Solubilities were determined by a gravimetric method except for white spirit for which the amount of COS produced by water-initiated polymerization of a white spirit solution, saturated with dione, was measured.

Effect of water. To gain further information on the effect of water, experiments were next carried out using fabric at various regains. These were obtained by drying *in vacuo* and then distilling in a known volume of water, which was sorbed by the dry fabric. In Figure 2 the optimum regain for shrinkproofing from white spirit is about 12–14%, no shrinkproofing occurring with a completely dry fabric. Water in the wool is therefore essential to

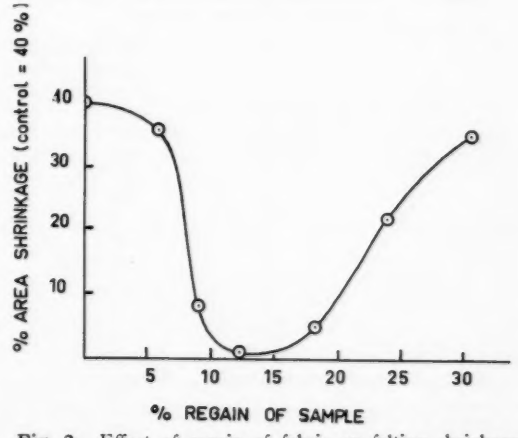

Fig. 2. Effect of regain of fabric on felting shrinkage. Fabric (4 g.) treated in 100 ml. white spirit containing 0.5 g. dione at 60° for 2 hr. with intermittent stirring.

[2] This observation led to the investigation of the potentialities of shrinkproofing in aqueous Na_2S solution. Good shrinkproofing (shrinkage = 2%, control = 40%) was obtained by wetting out the fabric in a 0.5% Na_2S solution at room temperature for 30 min. with a liquor : wool ratio of 25 : 1. The considerable amount of damage to the fabric was greatly reduced but not completely eliminated by saturating the solution with NaCl.

obtain shrinkproofing, and those solvents which have a high affinity for water (see Tables I and II) dehydrate the fabric to such an extent that good shrinkproofing cannot be achieved. Saturation of some of these solvents with water prevents dehydration of the fabric and allows shrinkproofing to occur (Tables I and II).

Effect of additive to white spirit. From Table III it can be seen that approximately 3% is the optimum amount of ethanol, at which point there is an appreciable increase in the solubility over that in 100% white spirit. Higher concentrations of ethanol cause decreased shrinkage resistance, possibly through dehydration of the fiber. Other additives were tried; those which increased the rate of shrinkproofing are shown in Table IV. Primary alcohols were much more effective than branched chain alcohols, and no shrinkproofing occurred in treatments at room temperature. Some of the solvents tested increased the solubility of dione in white spirit but did not allow shrinkproofing to occur.

Effect of inhibitors. Small quantities of benzoyl chloride inhibit the shrinkproofing reaction; see Table V. Similar results have been obtained with anhydrocarboxyglycine [14].

Effect of concentration of dione. Table VI shows that shrinkproofing occurs more rapidly as the dione concentration is increased from 0.2 to 0.6%. This is to be expected, since shrinkproofing is brought about by the deposition of polyglycine produced by a polymerization rate process involving the concentration of both water (the initiator) and dione (the monomer). Although the smallest amount of dione which will effectively shrinkproof a 4-g. sample of wool in 100 ml. white spirit at 80° for 1 hr. is 0.1 g., it is likely that an even smaller amount would be effective if given a longer time of treatment.

Effect of fabric pretreatment. Since hydroxyl ions cause very rapid initiation of polymerization of N-carboxy acid anhydrides [10], it was thought that pretreatment of the fabric with a dilute aqueous NaOH solution may allow more rapid reaction with dione. Fabric samples were wet out with 4 ml.

TABLE III. Shrinkproofing with Dione in White Spirit Containing Ethanol*

Ethanol, %, in white spirit	Area shrinkage, % (control = 40%)	Solubility of dione in solvent at 60°, %
0	14	0.06
1	12	—
2	3	0.08
3	2	—
4	5	—
6	8	—
8	15	—
10	33	—
50	39	—

* Fabric (4 g.) treated with 0.5 g. dione in 100 ml. solvent at 60° for 1 hr. with intermittent stirring.

TABLE IV. Shrinkproofing with Dione in White Spirit Containing Additional Solvent*

Solvent added	Solvent in white spirit, %	Area shrinkage, % (control = 40%) after treatment at 60° for 1 hr.	Area shrinkage, % (control = 40%) after treatment at 40° for 16 hr.
Nil	0	13	22
Ethanol	2	3	4
n-Butanol	2	4	2
n-Hexanol	2	3	—
Benzyl alcohol	2	1	2
Phenyl cellosolve	2	1	—
Toluene	10	9	—
Nitrobenzene	10	9	—
Chloroform	10	6	—
Chloroform	20	3	2
Chloroform	30	5	—
Chloroform	50	16	—

* Fabric (4 g.) treated with 0.5 g. dione in 100 ml. solvent for temperature and time indicated with intermittent stirring.

TABLE V. Inhibition by Benzoyl Chloride of Shrinkproofing with Dione*

Wt. benzoyl chloride, mg.	Area shrinkage, % (control = 40%)
0	2
2	17
10	32
20	35

* Fabric (4 g.) treated with 0.2 g. dione in 100 ml. white spirit at 80° for 1 hr. with intermittent stirring.

TABLE VI. Effect of Concentration of Dione on Shrinkproofing in Toluene*

Dione, % (wt./vol.)	Area shrinkage, % (control = 40%) after treatment for 1 hr.	2 hr.	5 hr.
0.2	13	18	1
0.4	4	3	1
0.6	2	1	2

* Fabric (4 g.) treated in 100 ml. toluene containing dione at 60° ± 5° with intermittent stirring.

0.025 *N* NaOH, allowed to condition, and then treated with intermittent stirring at 60° for 1 hr. in 100 ml. white spirit containing 0.5 g. dione. The fabrics were shrinkproof (shrinkage = 3%, control = 40%), whereas controls given only the pretreatment with aqueous NaOH showed no shrinkage resistance. A sample without pretreatment shrank 13% (see Table IV) under these conditions, showing that the NaOH pretreatment was effective in increasing the rate of shrinkproofing to about the same degree as the addition of 2% ethanol to the white spirit. A pretreated sample which was given the dione treatment for 16 hr. at room temperature (even with the addition of 2% ethanol to the white spirit) was not shrinkproof. As the primary amino group causes rapid initiation of polymerization of anhydrocarboxyglycine as compared with water [8], pretreatment of the fabric with primary amines or glycine was tried but found to be ineffective in increasing the rate of the shrinkproofing reaction. Likewise no change was observed by pretreatment of fabrics with buffers at pH 5, 7, 9, or 11.

Effect of time and temperature of treatment. The results given in Table VII show that it has not been possible to obtain shrinkproofing at room temperature even after prolonged treatment. Also treatments at temperatures above 80° are not possible because of discoloration of the fabric.

Summary of best conditions. After consideration of factors such as ease of treatment and cost, the best treatment appears to be that in which 4 g. fabric is immersed for 1 hr. in an intermittently stirred solution of 0.2 g. dione in 100 ml. white spirit containing 2% n-butanol at 60°. However, this treatment is too costly to be used in practice.

Bursting strength and abrasion resistance of fabrics. Fabric samples (4 g.) were treated with 0.3 g. dione in 100 ml. white spirit containing 2% n-butanol for 5 hr. at 60° (shrinkage = 1%, control = 40%) and conditioned at 65% RH and 20°. They showed a 9% increase of bursting strength over conditioned untreated fabric but there was no difference in the bursting strengths of the fabrics when wet out in water. The abrasion resistance of 12 approximately 0.2-g. samples of both treated and untreated fabric are recorded in Table VIII in terms of total weight lost and also number worn through after each 1000 rubs. About 50% more material is lost by rubbing the control than the treated. The treated withstands 1.5–2.0 times as much rubbing as the control before showing a hole, which is to be compared with a figure of 3.0 times obtained on wool shrinkproofed with anhydrocarboxyglycine [5].

TABLE VII. Effect of Time, Temperature, and Composition of Solution on Shrinkproofing with Dione

Temperature, °C.	Time (min.) to give effective shrinkproofing (area shrinkage ≤ 4%, control = 40%) under the following conditions	
	0.5 g. dione, 4 g. fabric, 100 ml. white spirit	0.5 g. dione, 4 g. fabric, 100 ml. white spirit solution containing 2 ml. n-butanol
about 25	*	*
40	*	16 × 60
60	120	60
80	11	—
90	<10†	—
100	< 5†	—

* Shrinkproofing could not be obtained under these conditions.

† Dione decomposed, giving brown spots on the fabric.

TABLE VIII. Resistance to Abrasion of Untreated and Shrinkproofed Fabric

Number of rubs	1000	2000	3000	4000	5000	6000
Wt. loss (mg.) of untreated	11.2	20.8	33.9	—	—	—
Wt. loss (mg.) of treated	7.3	15.0	23.3	30.3	39.6	55.4
Number worn through, untreated	0	0	4	—	—	—
Number worn through, treated	0	0	0	1	3	6

Glycine Content of Whole Fiber and Scale-Rich Material

The results in Table IX show that the dione-treated top shows an increase of 6.3 g. glycine/100 g. scale material as compared with only 1.1 g. glycine/100 g. whole fiber.

N-Terminal Amino Acid Content of Top and Polyglycine

The results in Table X are the means of two hydrolyses (four chromatograms) and show the effect of different times of hydrolysis in 6 *N* HCl on the yield of DNP-glycine obtained from DNP-wool and DNP-polyglycinated wool. It is clear that the maximum yield is obtained after about 12 hr.; likewise, the maximum yields of N-terminal serine,

threonine, and valine were obtained after this time of hydrolysis. In order to be able to correct for the decomposition of DNP-glycine during hydrolysis in HCl, two experiments were carried out in which additional DNP-glycine was added as recorded in Table X. The percent recovery of the DNP-glycine added in the 12-hr. hydrolysate = 100 (0.045 − 0.016)/0.046 = 63%; i.e., 37% decomposed. A similar calculation for the 16-hr. hydrolysate gives 49% decomposition. These values are considerably smaller than the 44% decomposition in 4 hr. and 64% decomposition in 8 hr. of DNP-glycine added to DNP-wool, determined by Middlebrook [23], and the 60% decomposition in an 8-hr. hydrolysis of DNP-glycine added to globin [24]. The smaller amount of decomposition in our work may be due to the fact that the HCl used for hydrolysis was more thoroughly purified (double distillation of A.R. reagent) and the reaction was carried out *in vacuo* in a sealed tube instead of under reflux.

For the 12-hr. hydrolysis the increase of the N-terminal glycine content due to polyglycine treatment is $100(0.071 - 0.016)/63 = 0.087$ mole glycine/10^4 g. DNP-wool. A similar calculation for the 16-hr. hydrolysis gives a value of 0.059 from which a mean figure of 0.073 ± 0.014 mole glycine/10^4 g. DNP-wool is obtained. In the absence of chain termination reactions [19], the number average degree of polymerization (DP_n) of the polyglycine attached to the wool is given by the equation

$$DP_n = (\text{g. glycine/g. wool})/(\text{g. N-terminal glycine/g. wool})$$
$$= .011 \times 91 \times 10^4/.073 \times 75 \times 100$$
$$= 18$$

The experimental error involved in the value of DP_n is calculated from the value of 0.011 ± 0.0038 g. glycine/g. wool (see Table IX) and the above figure of 0.073 ± 0.014 mole glycine/10^4 g. DNP-wool, which gives $DP_n = 18 \pm 10$.

The amount of DNP-glycine produced by hydrolysis of DNP-polyglycine in 6 *N* HCl for 1, 2, 3, 6, 12, and 16 hr. amounted to 2.5, 3.1, 5.1, 4.9, 5.6, and 4.6 mole/10^4 g. respectively. Once again the maxi-

TABLE IX. Glycine Content of Whole Fiber and Scale-Rich Material with Standard Errors

	Whole fiber		Scale material*	
	Untreated, mean of 8	Treated, mean of 5	Untreated, mean of 6	Treated, mean of 2
Glycine (mole/10^4 g. material at 65% RH and 20°)	5.1 ± 0.3†	6.5 ± 0.4	4.8 ± 0.2†	13.2 ± 0.6
Glycine (g./100 g. material at 65% RH and 20°)	3.8 ± 0.2	4.9 ± 0.3	3.6 ± 0.2	9.9 ± 0.5
Glycine inc. on treatment (g./100 g. material)	1.1 ± 0.38		6.3 ± 0.5	

* The scale material amounted to 0.6% of the total fiber weight.
† Figures obtained from [13].

TABLE X. N-Terminal Glycine Content of Untreated and Polyglycine-Treated Wool in Mole/10^4 g. Conditioned DNP-Wool*†

Time of hydrolysis, hr.	Samples hydrolyzed			
	DNP-wool	DNP-polyglycinated wool	DNP-wool + DNP-glycine (0.046 mole DNP-gly/10^4 g. DNP-wool)	DNP-wool + DNP-glycine (0.047 mole DNP-gly added/10^4 g. DNP-wool)
3	.013	.064	—	—
6	.015	.060	—	—
12	.016	.071	.045	—
16	.011	.041	—	.036

* The average 12-hr. hydrolysis figures for N-terminal serine, threonine, and valine of 0.017, 0.046, and 0.012 mole/10^4 g. dry wool are in reasonable agreement with the uncorrected values 0.012, 0.044, and 0.010 for Merino 64's virgin wool [28]. Weak spots due to alanine, aspartic acid, and glutamic acid were also identified on the paper, but were not measured.
† The weight increase due to dinitrophenylation of wool is 10% [28]; this figure is the same for polyglycinated wool.

mum yield of DNP-glycine was obtained after 12-hr. hydrolysis. Using the same correction factors for decomposition of DNP-glycine during hydrolysis as determined above, the corrected values for 12- and 16-hr. hydrolyses amount to 7.8 and 7.9 moles of N-terminal glycine/10^4 g. DNP-polyglycine respectively. The number average molecular weight (M_n) of the DNP-polyglycine therefore equals $10^4/7.9 = 1270$. As the dione polymerization was initiated by water, the structure of the DNP-polyglycine is $(NO_2)_2C_6H_3(NHCH_2CO)_{DP_n}OH$ from which one can calculate DP_n to be 19. This figure is considerably higher than the value of 5–8 found by Alexander et al. [2] on polymerization of dione in aqueous buffer solution at pH 9, but perhaps the presence of inorganic ions may affect DP_n, as was found in the polymerization of anhydrocarboxyglycine [7, 8]. Dione polymerized in distilled water at room temperature therefore gives polyglycine of about the same DP_n as that produced by polymerization on the wool fiber.

C-Terminal Amino Acid Content of Top

Duplicate hydrazinolyses gave results for the C-terminal amino acids serine, glutamic acid, and aspartic acid in both untreated and treated wool close to those obtained previously for Merino 64's [11]. The figures for C-terminal glycine in untreated and treated wool amount to 0.15 ± 0.026 and 0.21 ± 0.022 mole glycine/10^4 g. wool. The increase of the glycine content due to treatment amounts to 0.060 mole/10^4 g., which is in good agreement with the value of 0.073, the number of new N-terminal glycine residues produced by the treatment. Unfortunately, the experimental error involved in the hydrazinolysis experiments is so great that the difference of 0.060 is not significant (probability = 0.11).

ϵ-Amino Lysine Content of Top and Scale-Rich Material

Duplicate analyses showed that the amount of ϵ-NH_2 lysine groups in untreated and polyglycinated top and scale-rich material from both these sources is the same within experimental error at 2.3 mole /10^4 g. This agrees well with the value of 2.4 for the lysine content of the same sample of top obtained by the dinitrophenylation method [13].

Frictional Properties of Top

The average of the results from ten fibers was used to obtain each value of μ_1 and μ_2 shown in Table XI. Although there are differences in the figures obtained using different media, the same general conclusions can be drawn in each case; *viz.*, that μ_1 and μ_2 are increased but the D.F.E. is decreased by the treatment. This is in agreement with results obtained using fibers treated with polyglycine from anhydrocarboxyglycine [2, 5, 17].

Average Scale Shape Before and After Dione Treatment

The 50 values of α (see Figure 1) for each fiber before and after treatment were averaged (standard error $\gtrsim 2°$) and the difference obtained for each fiber. The mean value of this difference for the six fibers is recorded in Table XII, together with the

TABLE XII. Dimensions of the Idealized Scale Shape Shown in Figure 1 for Untreated and Polyglycinated Fibers

	Mean values for 6 fibers		Mean differences due to treatment
	Untreated	Treated	
α, °	40	37	3
β, °	131	134	3
Scale ht., μ	1.3	1.2	0.1

TABLE XI. Frictional Coefficients (with Standard Errors) of Untreated and Polyglycinated Lincoln 36's Top Using Various Media

	Medium in which fibers were measured					
	Air		Aqueous solution*		White spirit	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
μ_1†	0.32	0.42	0.35	0.66	0.35	0.54
μ_2	0.22	0.36	0.23	0.60	0.27	0.47
D.F.E.	0.19 ± 0.03	0.08 ± 0.01	0.21 ± 0.02	0.05 ± 0.01	0.13 ± 0.01	0.07 ± 0.01

* This consisted of 0.05 *M* borax + 0.02% Teepol in distilled water.

† μ_1 and μ_2 are the anti-scale and with-scale coefficients of friction, respectively; the directional frictional effect (D.F.E.) = $(\mu_1 - \mu_2)/(\mu_1 + \mu_2)$.

results of a similar analysis for β. There is no change in the average scale shape, as shown by optical microscopy, due to deposition of 1.7% by weight of polyglycine on the fibers (obtained by glycine analyses on treated top).

Discussion

Initiation of Polymerization by Water in the Fiber

There is a controversy in the literature as to whether the polymerization of anhydrocarboxyglycine on wool is initiated by the ϵ-amino groups of lysine [5] or by water present in the fiber [1, 2]. In the similar case of polymerization of dione all the evidence summarized below supports the thesis of initiation of polymerization by water.

No shrinkproofing with dione occurs under anhydrous conditions (Figure 2), or when a solvent is used which, because of its affinity for water, can dehydrate the fabric. In addition, there is an inverse correlation between the rate of shrinkproofing with dione and the solubility of water in the solvent used, except for benzene (Table II). The simplest explanation of the results in Figure 2 is that at low regains the water is so strongly bound at specific sites that very little is available to initiate polymerization, which is therefore slow. In the intermediate region, which includes that normally encountered in practice, sufficient water is available to allow polymerization on the surface, thus conferring shrinkproofing. As the regain continues to increase, so the amount of loosely bound water [30] increases, until it is possible for polymerization to occur some distance away from the fiber in the same way as in aqueous solution. It is also possible that more polymerization will occur inside the fiber rather than on the surface because of its highly swollen state.

The rate of shrinkproofing is not altered by pretreatment of the fabric with buffers in the range pH 5–11, although the ϵ-NH_2 lysine group would change from the charged form (which does not initiate polymerization of anhydrocarboxyglycine [7]) to the uncharged form (which does initiate polymerization in homogeneous solution) in this range.

Electron microscopy of dione-treated top shows an uneven surface deposit of polyglycine [25] in which it would be possible only for the initial monolayer to be initiated by ϵ-NH_2 lysine.

The increase of C-terminal glycine groups produced by the dione treatment is indicative of initiation by water (since there would be no change if initiation occurred by ϵ-amino lysine groups), but the results are not accurate enough to be conclusive.

Initiation by water would produce no change in the number of ϵ-amino lysine groups while it can be calculated that initiation by ϵ-amino lysine groups would produce a 27% decrease of the latter in the scales due to treatment. The results showed no change on treatment; hence it is concluded that water initiates the polymerization of dione on the wool.

Location of Polyglycine on the Fiber

Alexander et al. [2] attempted to locate the polyglycine produced by the polymerization of anhydrocarboxyglycine by dyeing treated and untreated fibers with Aqua Plastic Red followed by examination under the microscope. The untreated fibers dyed much more readily than the treated; hence no clear-cut conclusion could be drawn as to the location of the polymer. Makinson [21] found by microscopy and frictional tests that at least some of the polyglycine is located on the surface [22].

We have dyed dione-treated and untreated top with acid, basic, direct, and vat dyes and found the latter to dye more readily than the former in almost all cases, but the polyglycine could not be located by examination under the microscope. The results in Table IX show that there is a concentration of polyglycine in the surface layers. The best estimate available of the amount of material removed by descaling indicates that the maximum depth of abrasion amounts to $\geq 3\%$ of the diameter of the fiber [12, 14]. The scale material is therefore known to come from the outside 12% by weight of the fiber, assuming constant density of the fiber throughout its cross section. The 6.3-g. glycine increase/100 g. scale material is therefore equivalent to a figure of $6.3 \times 12/100 = 0.76$ (± 0.06) increase of glycine/100 g. whole fiber. It is clear that 0.76 (± 0.06) of the 1.1 (± 0.38) increase of glycine content of the whole fiber is concentrated in the scales. However, in view of the considerable standard errors involved, this must be taken only as the most probable result; indeed it may be that all the polyglycine is located in the scales [14]. Examination of the treated fibers by electron microscopy [25] shows that an uneven layer of polyglycine is located on the surface of the scales.

Mode of Shrinkproofing with Polyglycine from Dione

Since the dione polymerization is initiated by water on the wool, there is no possibility of forma-

tion of covalent bonds between polyglycine and the wool fiber. However, the protein-like structure of the polyglycine polymerized on the fiber (partly inside and partly on its surface) allows the formation of intermolecular hydrogen bonds which produce an uneven deposit of polymer. This deposit allows shrinkproofing to be obtained with a very small weight increase and without the necessity of pretreatment of the wool, as was required for effective shrinkproofing by all other methods investigated by Jackson [17]. The results in Table XII would seem to indicate that shrinkproofing can be obtained without alteration of the average scale shape, but Mrs. K. R. Makinson has brought to our notice the fact that it is geometrically impossible to see reentrant angles in the profile of a whole fiber; see also [20]. The results therefore serve to emphasize the limitations of the method used and show the need for electron microscopic examination of longitudinal sections of these fibers. Work along these lines is in progress in the Wool Research Laboratories.

It has been postulated that spot welding of fibers by polyglycine plays a part in shrinkproofing [1, 2, 5], but this seems to be most unlikely in this case for several reasons. The first is that optical and electron microscopic examination of fibers showed no evidence of uneven deposits of polymer of the magnitude required to effect spot welding (see also Makinson [22]). Second, the very small quantity (1%) of polyglycine required as compared with the amount of other polymers needed to effect shrinkproofing by spot welding (4–10% [17]) indicates that the mechanism in the former case is quite different. Finally, it is unlikely that 1% of polymer would be sufficient to effect shrinkproofing by spot welding, in the case of tops, where it might be expected that more spot welding would be necessary to immobilize the fibers than in fabric. We conclude that shrinkproofing is effected by increase of both μ_1 and μ_2 and by reduction of the D.F.E. of the fibers by deposition of polyglycine on and inside the scales.

Acknowledgments

The authors thank Dr. G. E. Rogers for several useful discussions and permission to use unpublished results. Dr. M. Lipson, Mrs. K. Rachel Makinson, and Mr. D. C. Shaw have contributed through discussions. We are grateful to Mr. A. R. W. Lee and staff for the physical testing of fabrics and Mr. H. Groll for carrying out the descaling and some of the amino acid analyses.

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Manuscript received August 3, 1959.

The Amino Acid Analysis of Cuticle-Rich Material from Wool

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Abstract

Cuticle material of various degrees of purity was obtained in yields ranging from 0.2% to 7.2% of the weight of the fiber by using descalers of different sharpness. Microscopic examination of the cuticle-rich material and the residual fibers abraded along one side showed that the material becomes richer in cuticle as the yield decreases. The material collected in 0.5–0.7% yield consists of about 50% cuticle and for the three samples of wool contains on the average 27% more proline and 40% less aspartic acid plus glutamic acid than the parent fibers. In one sample the cuticle-rich material is richer in glycine (39%) and in another richer in cystine (22%) than the parent fibers. The high proline content of the cuticle is consistent with its amorphous nature and the dearth of free carboxyl groups, interesting because of Lindberg's suggestion that the barrier to diffusion of dyes into the fiber is electrical in nature. However, other evidence indicates that the barrier is most probably the epicuticle, which constitutes < 2% of the material analyzed.

Introduction

A considerable amount of effort has been expended in attempts to determine the histological structure of the wool cuticle and its chemical composition. There are at least two main practical reasons for this. The first is that the felting shrinkage of woolen garments is thought to be due to the scale structure of the wool fiber cuticle. The second is that the cuticle is known to act as a barrier to the diffusion of dyes into the fiber. Clearly, a detailed knowledge of the structure of the cuticle could lead to improved methods of shrinkproofing and dyeing of wool.

By means of electron microscopy it has been established that there are three cuticle layers, epicuticle, exocuticle, and endocuticle [22], with the possibility of a fourth layer between the external epicuticle and the adjacent exocuticle [27]. Several attempts have been made to analyze the wool cuticle, which amounts to 5–10% by weight of fiber, after its separation from the bulk of the fiber by enzymic or chemical methods [7, 9, 11, 19, 20]. All these methods suffer from the disadvantage that it is impossible to estimate the amount of degradation of the cuticle which has occurred during its separation from the cortex. The abrasion technique used many years ago by King [14] to obtain descaled fibers does not possess this disadvantage, since it seems most unlikely that an appreciable amount of degradation would occur by heat generated during abrasion. The method was therefore improved such that cuticle-rich material could be collected in a glass descaler and analyzed [4].

Another problem is to establish the original location in the fiber of the so-called cuticle material. In the degradative methods this is obtained with some degree of satisfaction by optical or electron microscopic examination of the material, but in many cases there is the possibility of contamination with material originating from cortical cell membranes. With the abrasion method it is important to establish the depth of abrasion of the fiber. This can be checked by microscopic examination of cuticle-rich material from ring-dyed fibers [4] and by examination of the fibers which have been descaled along one side (see below).

The amino acid analysis of cuticle-rich material obtained by the abrasion technique is made by the dinitrophenyl method of Levy [15] because only 0.2 mg. of material is required for one analysis as against about ten times that amount required for the more accurate Moore and Stein method. This enables duplicate analyses to be made on 0.4–0.5 mg. of cuticle-rich material obtained by laborious descaling of several hundred fibers [4]. This paper gives a detailed account of the descaling technique and

the amino acid analysis of cuticle-rich material from three samples of wool. The amide nitrogen results [5] are also included in the discussion of the composition of the wool cuticle.

Experimental

Materials

The cleaning of the three samples of wool is described elsewhere [5]. The 6 *N* HCl used for hydrolysis of the protein was concentrated A.R. HCl fractionated once and then distilled a second time just before use. Samples of *meso*-lanthionine (Lan) and L-citrulline (Cit) were kindly supplied by Dr. G. Tauber of this laboratory and Dr. G. E. Rogers of the Division of Protein Chemistry, Melbourne, respectively; all other amino acids were of Laboratory or A.R. grade.

Procedure for Preparation and Estimation of Dinitrophenyl Amino Acids

The amino acids were quantitatively dinitrophenylated by the method of Sanger [26] with slight modifications as previously described [3]. They were run on two-dimensional paper chromatograms using Whatman No. 1 paper and either or both of the following solvent systems. With the first system [15] the "toluene" solvent was used first with upward development for 40 hr. and, after the paper was dried for about 2 hr. at 40–50°, the phosphate buffer (0.8 *M* NaH_2PO_4, 0.4 *M* Na_2HPO_4) at pH 6 was used in the second dimension for 40 hr., also by the ascending method. The second system used a paper buffered with 0.1 *M* phthalate buffer (pH 5) and the solvent 2-methylbutan-2-ol saturated with phthalate buffer running downwards for 40 hr. [10]. After being dried, the paper was developed in the second dimension with the phosphate buffer (pH 6) by the ascending method for 40 hr. The position of the dinitrophenyl (DNP)-amino acid spot was noted relative to that of 2:4-dinitrophenol and 2:4 dinitroaniline; the spot was excised, together with three paper blanks, and weighed approximately. The color was eluted with 5 ml. 2% $NaHCO_3$ for 30 min. at room temperature and the optical density of the solutions measured at 360 mμ (385 mμ for DNP-proline) in 1-cm. matched cells of a Unicam spectrophotometer. The small blank correction (usually about 0.01/100 mg. of paper) was subtracted from the observed optical density before calculation of the molar extinction coefficient.

Dinitrophenylation of arginine and cysteic acid yielded DNP-amino acids which cannot be extracted from aq. acid solution by ether and so n-butanol (3 × 5 ml.) was used [6]. The n-butanol was evaporated and the DNP-amino acid dissolved in acetone, made up to volume, and aliquots applied as spots to Whatman No. 1 paper. The paper was run in one dimension by the descending method for 16 hr. using the top n-butanol-rich layer of the mixture n-butanol–acetic acid–water (4:1:5, vol./vol.). The spots due to the DNP-amino acids were excised, their optical density measured, and the molar extinction coefficient calculated.

The dinitrophenylation of histidine and its separation led to complications because it gave mixtures of α-mono-DNP-histidine and bis-DNP-histidine and caused problems in the extraction of these compounds from aq. solution. In confirmation of Levy [15] it was found that dinitrophenylation at 40° in aq. solution for 20 min. produced only α-mono-DNP-histidine. Thus chromatography of the ether and n-butanol extracts of the aq. acid reaction mixture in one dimension using the phosphate or the n-butanol–acetic acid–water solvents showed that no bis-DNP-histidine was present and all the α-mono-DNP-histidine was extracted into the n-butanol layer. Dinitrophenylation for 16 hr. by Sanger's method converted almost all the histidine to bis-DNP-histidine, as shown by chromatography of the ether and n-butanol extracts, but only 20% of the material was extracted by the 5 × 5 ml. extractions with ether. Mills [23] found that quantitative extraction with ether was possible only by a continuous method. The normal dinitrophenylation for 3 hr. by Sanger's method gave 20% of bis-DNP-histidine

Fig. 1. Two-dimensional chromatogram of DNP-amino acids using 2-methylbutan-2-ol followed by phosphate buffer as described in the text.

in the ether extract and 60% in the n-butanol extract together with 20% of α-mono-DNP-histidine, the results being calculated on the assumption that the molar extinction coefficients of both products were equal. No difficulty was experienced in the quantitative dinitrophenylation of L-citrulline but, as with histidine, it was found that only 18% of DNP-citrulline was extracted by ether in the normal five extractions and the remaining 82% by the subsequent n-butanol extractions.

Chromatographic Separation of Dinitrophenyl-Amino Acids [1]

The "toluene"–phosphate system of chromatography gave irreproducible results for bis-DNP-Lys and bis-DNP-Tyr. In addition, the separation between DNP-Asp and DNP-Glu and DNP-Val, DNP-Leu, and DNP-Ileu was usually incomplete. However, the phthalate–phosphate system gave much more consistent results for Lys and Tyr as well as a better separation of DNP-Asp and DNP-Glu. As there is apparently no reference in the literature of the use of this system, a map of the distribution of DNP-amino acid spots is given in Figure 1. The composite spot bis-DNP-Cys + bis-DNP-Lan + bis-DNP-His effectively reduced to bis-DNP-Cys in hydrolysates of untreated wool, since bis-DNP-Lan was small and the amount of bis-DNP-His expected on the chromatogram as a result of ether extraction of the aq. solution was $\geq 20\%$ of $0.60 = 0.12$ mole/10^4 g. wool [28]. These three materials can be separated by the "toluene"–phosphate system. In untreated wool there is about 2.3 mole/10^4 g. of Lys (see below) and 0.32 mole/10^4 g. of CySH [13], but because the molar extinction coefficient of bis-DNP-CySH is only two-thirds that of bis-DNP-Lys, the error made in neglecting the former in the composite spot bis-DNP-Lys + bis-DNP-CySH is only about 10%. These spots cannot be separated by the "toluene"–phosphate system. The weak spots due to DNP-Phe and DNP-Met were completely masked by the strong spot of 2:4-dinitrophenol, hence were not usually determined, although DNP-Phe was estimated in a few cases from "toluene"–phosphate chromatograms. No attempt was made to isolate the components of the composite spot DNP-Val + DNP-Leu + DNP-Ileu and all results are given as a total value; the same procedure was used where there was considerable overlap of DNP-Asp and DNP-Glu.

The DNP-amino acids extracted by n-butanol were run by the descending method for 16 hr. using the n-butanol-rich layer of the solvent n-butanol–acetic acid–water (4:1:5, vol./vol.). The distribution of the spots was similar to that given in Figure 2 of Fraenkel-Conrat, Harris, and Levy [10], except that bis-DNP-His was found to run faster than DNP-Arg.

Molar Extinction Coefficients of Dinitrophenyl-Amino Acids

The molar extinction coefficients calculated from the experiments with two-dimensional chromatograms amounted to 1.25 ($\pm$ 0.068) $\times 10^4$ for Ala, Asp, Cit, Glu, Gly, Leu, Pro, Ser, Thr, and Val; 1.92×10^4 for Cys (bis) and Lan (bis); 1.85×10^4 for Lys (bis); and 0.73×10^4 for Tyr (bis); those for the one-dimensional chromatogram (Arg and $CySO_3H$) were unchanged from the previous figure of 1.47×10^4 [3]. The above figures allow for the fact that the recovery of all the DNP-amino acids (except Tyr) from two-dimensional chromatograms is only 85% of that obtained from one-dimensional chromatograms [3]. This loss of 15% of material in the second dimension has not been investigated further because it is constant in amount and similar losses have been observed before [3, 5]. The 50% loss of bis-DNP-Tyr in the second dimension leads to large errors in Tyr analyses, as shown below and found by Levy [15].

Production of Cuticle-Rich Material of Various Degrees of Enrichment

A sketch of the descaler and description of its mode of operation have already been given [4]. By varying the sharpness of the abrasive edge and the number of passes of fiber across it, it was possible to abrade the fiber to different extents. The sharpest cutting edge was produced by leaving the chisel-edge rough rather than fire-polished. Using this edge it was possible, by continued rubbing back and forth without turning the fiber, to obtain up to 10% of its weight before breakage occurred, or a yield of about 1.5% by one pass of the fiber. A blunter edge was obtained by fire-polishing the top of the central rod and making a cut across it with a sharp glass-knife [4]. The yield of cuticle-rich material in this case was 0.5–0.8%, but after being

[1] For explanation of the abbreviations used for the amino acids see *Biochem. J.* **55**, 5 (1953).

used for about 10 experiments the edge became so blunt that only about 0.2% of material was removed.

Microscopical Examination of Cuticle-Rich Material and Residual Fibers

As previously described, fibers that were ring-dyed to a depth of 3% of the diameter were passed through the descaler and the cuticle-rich material examined under the microscope [4]. It was found that the material produced in a yield of about 1.5%, using the sharpest abrasive edge, consisted of long, thin strips often only partly dyed. However, that produced in a yield of 0.5–0.8%, using the blunter abrasive groove, consisted almost entirely of fine dyed pieces, showing that it came from the outside of the fiber.

Untreated and descaled 1-mg. samples (30) of Lincoln 36's virgin root wool were dyed in 30 ml. 0.01% methylene blue in 0.04 *M* phosphate buffer at pH 7 for 5 min. at room temperature and washed 6 times with distilled water. The fibers were dried and about 100 snippets examined under the microscope. A count was made of the number of snippets in each of four different categories. These are described as (1) undyed, (2) dyed in the manner recorded in Figure 1 (Classes 1–4) of Whewell and Woods [30] and showing no lines of dye along the fiber, (3) showing lines of dye along the fiber with evidence of slight removal of scale edges in the dyed strip in some cases, and (4) exhibiting considerable surface-damage, as shown by strips of material projecting from the surface of the fiber or irregularities in the fiber profile, accompanied by heavy dyeing. The results of the count are recorded in Table I.

It is not possible to obtain a quantitative estimate of the percentage of abraded snippets because it is not known how much abrasion is necessary before it is shown up by the methylene blue damage test. For this reason there has been no attempt to classify those snippets which fall into Class 2 as damaged or undamaged on the basis of the extent of dyeing of the fiber [30]. As would be expected, the degree of abrasion of the fibers, as shown by the number falling in Classes 3 and 4, increases with increasing severity of descaling. There appears to be very little removal of cortex in those fibers falling into Class 3, whereas in Class 4 a considerable amount must be removed. However, as only 4% of fibers fall into the latter class in the normal descaling (0.5–0.8% yield), there is not a great deal of contamination of cuticle-rich material with cortex.

TABLE I. Percentage of Fiber Snippets from Untreated and Descaled Lincoln 36's Root Wool Classified According to Extent of Damage

% Yield of cuticle-rich material from fiber	Class number			
	1	2	3	4
0 (untreated)	72	28	0	0
0.2	52	36	10	2
0.7	49	30	17	4
1.8	22	30	40	8
7.8	33	11	28	28

Ultra-thin cross sections of fibers abraded to the extent of 1.5% and 0.5% were examined under the electron microscope by Dr. G. E. Rogers, Division of Protein Chemistry, Melbourne. It was not possible to make a quantitative estimate of the relative amounts of cuticle and cortex removed, but it was found that more fibers showed removal of a portion of the cortex in the former than in the latter descaling. With the latter many cross sections showed no signs of abrasion, although some still showed removal of cortical material with the cuticle.

Procedure for Amino Acid Analysis of Cuticle-Rich Material.

The descaler was cleaned with chromic acid, washed 20–30 times with water, and finally washed with glass-distilled water. It was dried and then conditioned to constant weight ($\pm 5 \times 10^{-3}$ mg.) at 65% RH and 20°. Fibers were rubbed across the abrasive edge until more than 0.4 mg. of material had collected, after which the descaler was again weighed to constant weight. It was placed inside a large Pyrex test tube, previously cleaned as described for the descaler, and 2 ml. of twice-distilled 6 *N* HCl added. The tube was sealed under vacuum and heated at 105° for 16 hr. in an oven. It was then opened, the HCl evaporated carefully, and 1 ml. of 0.5 *M* $KHCO_3$ added, followed by a solution of 25 mg. of 1-fluoro-2:4-dinitrobenzene (FDNB) in 2 ml. absolute ethanol. The solution was shaken for 3 hr. at room temperature, 5 ml. 0.5 *M* carbonate buffer (pH 9) added, and the bulk of the ethanol evaporated at the water pump. The solution was extracted with ether (3 × 10 ml.) and the combined ether extracts washed once with 10 ml. of carbonate buffer. The combined aq. solutions were acidified with HCl, extracted with ether (5 × 10 ml.) and then n-butanol (3 × 5 ml.). The ether solution was divided into two parts which were evaporated to dryness; the yellow material of each was dissolved

TABLE II. Amino Acid Composition of Lincoln 36's Virgin Wool (Base and Tips) and Cuticle-rich Material of Various Degrees of Enrichment (Mole Amino Acid/10^4 g. Material at 65% RH and 20°) with Standard Errors

Amino acid	Tips	Base	Cuticle-rich material obtained in the following yields, % by wt. of fiber			
			7.2	1.6	0.5	0.25
Ala	4.5	4.6 ± .1	4.7	4.6	4.9 ± .5	4.8
Arg	4.4	4.9 ± .2	4.3	4.2	4.2 ± .7	3.6 ± .1
Asp + Asp(NH_2)	16.6 ± .4	14.1 ± .6	4.5	13.2	10.3 ± 1.3	5.0
Glu + Glu(NH_2)			9.7			8.1
Cys	4.1	4.5 ± .2	5.0	5.2	4.6 ± .6	5.2 ± .2
$CySO_3H$	0.44	0.11	0.3	0.3	—	0.3
Gly	5.0 ± .5	4.3 ± .1	5.0 ± .3	5.0 ± .1	6.0 ± .4	5.4 ± .1
Ileu + Leu + Val	13.9	14.4 ± .8	13.8	14.0	16.1 ± 1.6	11.9 ± .4
Lys	1.7 ± .1	2.1 ± .2	2.4	2.4	2.1 ± .3	2.0
Tyr	2.1 ± .2	3.4 ± .3	2.8	3.1	3.3 ± .8	2.0 ± .2
Pro	6.5	6.4 ± .2	7.6 ± .7	7.8 ± .2	8.5 ± .7	8.2 ± .1
Ser	9.9	9.6 ± .9	10.7	10.6	10.3 ± 1.1	11.5 ± .3
Thr	6.0	5.7 ± .4	5.7	5.6	5.6 ± .8	4.9
Total	75.1	74.1	76.2	75.7	75.9	72.6
No. of hydrolyses	3	6	2	4	4	3

TABLE III. Percentage Deviations of Amino Acid Content of Tips or Cuticle-Rich Material from That of Lincoln 36's Base Which are Significant at the 1% Probability Level

Amino acid	Tips	Cuticle-rich material obtained in the following yields, % by wt. of fiber			
		7.2	1.6	0.5	0.25
Arg	—	—	—	—	−26
Asp + Asp(NH_2)	+17*	—	—	−28*	—
Glu + Glu(NH_2)					
$CySO_3H$	+300	—	—	—	—
Gly	—	+16	+17	+39	+26
Tyr	−39	—	—	—	−41
Pro	—	—	+21	+33	+27

* Significant at the 5% probability level.

in acetone and applied as spots on two-dimensional chromatograms. They were run using the phthalate–phosphate system; the spots due to the various amino acids were cut out and 5 ml. 2% $NaHCO_3$ added. After the yellow solution stood at room temperature for 30 min., its optical density was measured at 360 mμ (385 mμ for DNP-Pro) in a Unicam spectrophotometer. In a similar way the n-butanol solution was evaporated to dryness, the residue dissolved in acetone, divided into two parts, and applied to a one-dimensional paper. This was run by the descending method using the n-butanol–acetic acid–water solvent, the spots due to DNP-$CySO_3H$ and DNP-Arg cut out and measured as described above. After correction of the optical density for the small paper blank, the concentration of each amino acid in mole/10^4 g. material at 65% RH and 20° was calculated using the values of the molar extinction coefficients given below. Tryptophan, histidine, and methionine, which occur only to a small extent in wool [28], were not estimated. Phenylalanine was determined in early work in which the toluene–phosphate solvent was used, and the results obtained showed reasonable agreement with those of Simmonds [28]. However, it could not be estimated using the phthalate–phosphate system (see above). Similar analyses were made on whole fibers of Lincoln 36's and Corriedale 46's wool obtained from the same source as those from which the cuticle-rich material had been derived.

Results

Table II gives detailed results for the amino acid analysis of root wool (base), tips, and material, enriched to various degrees with cuticle obtained by the descaling of root wool. The values of $CySO_3H$ for tips and base were obtained by separate experiments starting with 3 mg. of wool, but as it was not possible to obtain such a large amount of cuticle-rich material the $CySO_3H$ values for the latter are approximate and given as a maximum. A similar separate experiment to determine citrulline in 0.4 mg. cuticle-rich material (0.8% by weight of the fiber) gave a negative result, showing that the citrulline content is < 0.2 mole/10^4 g. cuticle-rich material: Rogers [25] found a considerable amount in the inner root sheath of hair follicles. The ash content of Lincoln 36's base and cuticle-rich material there-

from (obtained in 0.8% yield) was determined by Dr. W. Zimmermann, Microanalytical Laboratory, C.S.I.R.O., Melbourne, to be 0.60% and 2.34% respectively. Table III summarizes the significant differences in amino acid composition of tips or cuticle-rich material from Lincoln 36's base.

Cuticle-rich material (0.6–0.7% of whole fiber) was obtained from two other samples of wool; the results of the analyses are given in Table IV. The amino acid analysis of Corriedale 46's whole fiber agrees quite favorably with the results obtained by Simmonds [28] on Corriedale 56's wool using the Moore and Stein technique. The over-all mean standard error of the results shown in Tables II and IV amounts to 6.9%. In Table V the significant differences between amino acid content of cuticle-rich material and whole fiber for the three different samples of wool are given.

Discussion

Three methods have been used in an attempt to estimate the relative proportion of cuticle and cortex in the material produced by descaling. The first one is to pass fibers, ring-dyed to a known depth, through the descaler and examine the cuticle-rich material produced under the optical microscope [4]. In this way it is found that fibers ring-dyed to a depth of 3% of the diameter produce cuticle-rich material consisting almost entirely of small dyed pieces when 0.5–0.8% by weight of fiber is removed.

The second method is to descale fibers which have a layer of polyglycine on their surface (Bradbury, J. H. and Shaw, D. C., unpublished results). The sample in question contains 2% by weight of polyglycine, half of which is located as a fairly uniform deposit about 1000 Å thick on the surface of the fibers (Rogers, G. E., unpublished results). On descaling the fiber in 0.5% yield, the glycine figure is 32.4 mole/10^4 g. as compared with 4.8 mole/10^4 g. for an untreated fiber. If the reasonable assumption is made that half of the polyglycine is located in the cuticle layer, it can be calculated that the average depth of descaling amounts to 2.4% of the diameter of the fiber. This figure is a maximum average value, since it would be decreased if some polyglycine is located in the cortex. The third method involves

TABLE V. Percentage Deviations of Amino Acid Content of Cuticle-Rich Material, Obtained in 0.5–0.7% Yield, from That of Whole Fiber Which are Significant at the 1% Probability Level

Amino acid	Lincoln 36's virgin wool, base	Lincoln 36's processed to top form	Corriedale 46's virgin wool, base
Asp + Asp(NH_2)	−28*	−14†	−24
Glu + Glu(NH_2)		−13	−23*
Cys	—	+22	—
Gly	+39	—	—
Pro	+33	+21	+27*

* Significant at the 5% level.
† Probability $P = 0.068$, due to poor separation of DNP–Glu and DNP–Asp.

TABLE IV. Amino Acid Composition of Whole Fibers and Cuticle-Rich Material (Mole Amino Acid/10^4 g. Material at 65% RH and 20°) with Standard Errors

Amino acid	Lincoln 36's, processed to top form		Corriedale 46's virgin wool, base		Corriedale 56's virgin wool, base, calc. from [28]
	Whole fiber	Cuticle-rich material (0.6% of whole fiber)	Whole fiber	Cuticle-rich material (0.7% of whole fiber)	
Ala	4.8 ± .1	4.8 ± .3	4.4 ± .2	4.6 ± .2	4.6
Arg	4.8 ± .2	5.4 ± .4	5.4 ± .3	5.9 ± .6	4.8
Asp + Asp(NH_2)	4.9 ± .3	4.2 ± .1	4.8 ± .2	3.6 ± .1	5.1
Glu + Glu(NH_2)	8.5 ± .2	7.4 ± .3	8.5 ± .9	6.6 ± .4	10.2
Cys	3.4 ± .2	4.1 ± .1	3.7 ± .6	4.2 ± .2	3.6
Gly	5.1 ± .3	4.8 ± .3	5.2 ± .1	5.2 ± .3	6.7
Ileu + Leu + Val	15.2 ± .4	13.9 ± .9	15.3 ± 1.0	15.3 ± .9	13.0
Lys	2.4 ± .1	2.6 ± .2	2.3 ± .1	2.3 ± .1	2.0
Tyr	3.9 ± .3	3.1 ± .3	3.7 ± .3	3.6 ± .4	3.3
Pro	6.1 ± .3	7.3 ± .3	6.3 ± .3	8.0 ± .7	5.8
Ser	8.9 ± .4	9.2 ± .7	8.7 ± 1.5	10.1 ± 1.4	8.1
Thr	5.4 ± .1	4.7 ± .4	5.3 ± .3	5.0 ± .2	5.1
Total	73.4	71.5	73.6	74.4	72.3
No. of hydrolyses	8	6	4	4	—

the optical and electron microscopic examination of the residual fibers after descaling, from which it is possible only to draw the qualitative conclusion that some cortex is removed during descaling.

Ames [1] found the thickness of the cuticle in Merino wool to be about 5000 Å, Appleyard and Greville [2] gave a figure of $\geqslant$ 6600 Å for Lincoln and Leicester wool, and measurements of cuticle thickness of the sample of Lincoln 36's top used in this work gave an average value of about 5000 Å (Rogers, G. E., unpublished results). Using this figure together with the assumptions that the fiber is circular in cross section (diameter = 40 μ) and that a cap of material is cut off with a depth, at its center, of 3% of the diameter, it can be calculated that 56% of this cap is cuticle material. It is therefore reasonable to suppose that the material produced in 0.5–0.8% yield by descaling contains about 50% of cuticle.

Consden, Gordon, and Martin [8] established qualitatively the presence of cysteic acid in wool tips, and it is now shown in Table II that there is four times as much in the tips as in the base of Lincoln 36's virgin wool. In addition, there appears to be more Asp + Asp(NH_2) + Glu + Glu(NH_2) and less tyrosine in the tips than in the base of the fiber, although the tyrosine result is open to some doubt in view of unknown sources of error in the analytical procedure in this case (see above and Levy [15]).

There is about four times as much ash in the cuticle-rich material as in the whole fiber of Lincoln 36's virgin wool base. This may be due to contamination with fragments of glass from the descaler or inadvertent contamination of the exterior of the fibers with inorganic dust or may be due to residual suint or other material produced by the sheep which had not been removed during cleaning.

In Table III the results for Pro and to a lesser degree Gly and Asp + Asp(NH_2) + Glu + Glu (NH_2) show increased differences between the amino acid content of whole fiber and cuticle-rich material as the yield of the latter progressively decreases from 7.2 to 0.5%. This is consistent with the idea that the material analyzed is becoming progressively richer in cuticle in this series. However, the trend is not continued as the yield of cuticle-rich material is further reduced to 0.25%. The reason for this is not clear, but may possibly be due to a partial fractionation of the cuticle layers. Confirmation of this result using the other samples of wool has not been attempted because of the extremely laborious nature of the work; about 800 fibers need to be descaled in order to obtain about 0.4 mg. of cuticle-rich material in a yield of 0.25%.

In Table V it is seen that the cuticle-rich material is consistently rich in proline and poor in Asp + Asp(NH_2) + Glu + Glu(NH_2) for the three samples of wool and is also rich in glycine in one case and cystine in another. This indicates substantial differences between different types of wool. The consistently high proline content of the cuticle has already been noted [4] as a possible contributing factor towards its amorphous nature [12, 20, 31] because of the known difficulty of arranging proline in an ordered structure [29].

The consistently low values of Asp + Asp(NH_2) + Glu + Glu(NH_2) in the cuticle can best be considered in conjunction with the amide nitrogen results [5]. These are summarized in Table VI, where it is shown that the cuticle is consistently poor in aspartic acid + glutamic acid. On the average the cuticle-rich material contains 40% less free carboxyl groups than the whole fiber. Examination of the number of basic groups in whole fiber and cuticle-rich material (0.5% yield) in Tables II and IV shows that both arginine and lysine are constant within experimental error over the series of

TABLE VI. Content of Acidic Amino Acids and Acid Amides in Three Different Samples of Wool and Cuticle-Rich Material Therefrom (Mole Amino Acid/10^4 g. Material at 65% RH and 20°) with Standard Errors*

	Lincoln 36's virgin wool, base		Lincoln 36's, processed to top form		Corriedale 46's virgin wool, base	
Amino acid	Whole fiber	Cuticle-rich material	Whole fiber	Cuticle-rich material	Whole fiber	Cuticle-rich material
Asp + Asp(NH_2) + Glu + Glu(NH_2)	14.1 ± .6	10.3 ± 1.3	13.4 ± .4	11.6 ± .3	13.3 ± .9	10.2 ± .4
Asp(NH_2) + Glu(NH_2)	7.0 ± .2	7.2 ± .5	7.4 ± .4	7.4 ± .6	7.3 ± .2	6.1 ± .1
Asp + Glu	7.1 ± .6	3.1 ± 1.4	6.0 ± .5	4.2 ± .6	6.0 ± .9	4.1 ± .4

* The yield of cuticle-rich material was 0.5–0.7% and the figures for Asp(NH_2) + Glu(NH_2) were obtained from [5].

results with a mean value of 7.4 mole (arginine + lysine)/10^4 g. conditioned material. This value excludes histidine, the other basic amino acid in wool, which is not determined since it is present to the extent of only about 0.5 mole/10^4 g. (calculated from Simmonds [28]). In the unlikely event of the histidine content of cuticle-rich material being very different from that of the whole fiber, the total number of basic groups of both would still equal 7.9 within experimental error. On the other hand, it is calculated from Table VI that the mean number of acid groups of whole fiber and cuticle-rich material amounts to 6.4 and 3.8 mole/10^4 g. conditioned material respectively.

This lower concentration of free carboxyl groups in the cuticle might possibly be responsible for the surface barrier to the diffusion of dyes and acids into wool fibers [16, 21, 24], particularly as Lindberg [16, 17] has postulated that the barrier is electrical in nature. However, there is some evidence that the barrier does not consist of the whole cuticle of thickness around 6000 Å [1, 2] but only the epicuticle, which is the outside, highly resistant layer of thickness around 100 Å [18]. First, there is the occurrence of blotchy dyeing of sound fibers after gentle rubbing in the hand, which is most simply explained as due to cracking the thin surface layer of epicuticle, since this would probably be too mild a treatment to affect the whole cuticle [30]. Also, the extreme chemical inertness of the epicuticle as compared with the other cuticle layers [22] seems to indicate that it is the barrier. Finally, the epicuticle is undoubtedly responsible for the low coefficient of friction and low degree of wettability of the fiber, since these are surface properties, and they are altered very considerably by the alcoholic potassium hydroxide treatment which removes the barrier to dyeing [17].

It therefore appears likely that the epicuticle is the barrier to diffusion of dyes and acids into the fiber, but its mode of action cannot be known with certainty until it can be separated essentially unchanged from the fiber and analyzed. The technique described in this paper is inadequate for the task, since the cuticle-rich material separated contains at most 2% of epicuticle.

Acknowledgments

The author thanks Dr. G. E. Rogers for permission to quote unpublished results and for several stimulating discussions. Mr. H. Groll laboriously prepared the samples of cuticle-rich material and carried out the amino acid analyses.

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Manuscript received September 15, 1959.

Tryptophan in Wool

Part I: Determination of the Tryptophan Content of Wool

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Introduction

The determination of the amount of a given amino acid in wool is normally carried out after acid hydrolysis. Tryptophan, however, is unstable to the conditions usually used for acid hydrolysis, and this had led to the development of methods for its determination using alkaline hydrolysis. Spies and Chambers [12] have, however, shown that the determination of tryptophan in casein, after alkaline hydrolysis, is unreliable unless special precautions, such as the use of an atmosphere of hydrogen, were taken. They found that there is reaction of tryptophan with serine, threonine, and cystine during hydrolysis; to avoid this they developed a method for the estimation of tryptophan in intact proteins by reaction with *p*-dimethylamino-benzaldehyde in 19 *N* sulfuric acid.

As wool contains larger amounts of serine, threonine, and cystine than casein, results for the tryptophan content based on methods involving alkaline hydrolysis are likely to be less reliable than those for casein.

In a preliminary note [4] we reported the tryptophan content of wool determined by a modification of the Spies and Chambers method for the estimation of tryptophan in intact proteins. This paper is a fuller account of this work.

Experimental Methods

Materials

The wool used for the experiments to determine the optimum conditions for the tryptophan analysis was a knitted fabric made from a 2/26's 64's quality wool. Before use, the wool was extracted with aldehyde-free ether and given a scour in a solution of Lissapol N (ICI) and salt at 30° C. followed by a thorough rinse in water.

A number of samples of raw wools from various sources were also examined; these were purified by solvent extraction and aqueous scouring as described above. Any dust, burrs, etc. were removed by shaking and hand sorting. The fiber diameter of these wools was determined on a section across a single lock of wool fibers at the root end. The tryptophan content was determined on a 30-mg. sample taken from both sides of the section used for fiber diameter. There was a minimum of 100 fibers in the sample for fiber diameter; in the case of the finer quality wools, 60–70% of the fibers had a diameter within $\pm 2\ \mu$ of the average diameter. The coarser fibers were less homogeneous, approximately 40–50% of the fibers being within $\pm 2\ \mu$ of the average diameter.

The moisture content of the wool was determined by drying a 1-g. sample, taken at the same time as the sample for analysis, to constant weight at 105–110° C.

The chemicals used were of Analar or similar specification. The amino acids used were obtained from British Drug Houses Limited.

Preparation of Calibration Curves

Tryptophan is readily attacked by strong sulfuric acid solutions (c. 19 *N*) this means that care has to be taken in the preparation of the calibration curve to prevent decomposition of the tryptophan. We have found that if the standard tryptophan solution is added slowly with agitation to the *p*-dimethylamino-benzaldehyde, previously dissolved in the strong sulfuric acid, linear calibration curves were obtained and there appeared to be no loss of tryptophan.

It was found that the calibration curve was dependent on the sulfuric acid concentration; a calibration curve was prepared for each concentration of sulfuric acid.

General Method for the Determination of Tryptophan in Wool

Wool (30 mg.) of known moisture content was added to a solution of the aldehyde in 10 ml. sulfuric acid solution and the mixture allowed to stand in the dark at room temperature with occasional shaking until the wool dissolved. This took about seven days.

TABLE I

Wt. of aldehyde used, mg.	Tryptophan content, %
20	0.96
60	0.98
100	0.98
200	0.97
300	0.93

TABLE II

Acid concentration, *N*	Tryptophan content, %
17.1	0.96
18.1	0.98
18.9	0.98
21.2	0.99
23.0	0.99
24.5	1.05

The blue color of the tryptophan *p*-dimethylamino-benzaldehyde condensation product was then developed by the addition of 0.1 ml. 0.01 *M* sodium nitrite solution. The color intensity was estimated after 30 min. with a Spekker photoelectric adsorptiometer using Chance OR2 filters. The majority of the results were checked using Chance OY2 and Ilford Spectrum Orange 607 filters; the tryptophan contents obtained with the three filters were identical in each case, which suggests that there is little or no interference from stray colors.

All results are expressed as grams of tryptophan per 100 gram of dry protein.

Results

Effect of Aldehyde Concentration

The effect of the aldehyde concentration on the tryptophan content of the samples of wool fabric using 18.1 *N* sulfuric acid is given in Table I. The reduction of the tryptophan content with the highest amount of aldehyde used is most probably due to interference from the pale yellow color of strong solutions of *p*-dimethylamino-benzaldehyde in 18.1 *N* sulfuric acid.

In all further work the amount of aldehyde used was 100 mg.

Several different samples of aldehyde were used, varying from unpurified reagent grade to recrystallized Analar material. In every case the tryptophan content of the wool fabric was 0.98–0.99 g./100 g. dry wool.

TABLE III. Effect of Temperature

Temperature, °C.	Approx. time for the wool to dissolve	Tryptophan content, %
0	9 weeks	1.01
18	8 days	0.98
30	4 days	0.98
40	2½ days	0.94
60	6½ hr.	0.91

Effect of Acid Concentration

Table II shows the effect of sulfuric acid concentration on the tryptophan content of wool fabric.

The high results obtained with 24.5 *N* sulfuric acid may be due to interference, as a brownish green color was obtained instead of the normal blue color of the tryptophan-aldehyde complex. Addition of amino acids other than tryptophan present in wool to 24.5 *N* sulfuric acid showed that a brown color was obtained only with tyrosine, which suggests that the interference with the tryptophan analysis may be due to reaction of tyrosine with 24.5 *N* sulfuric acid.

In addition to these experiments using sulfuric acid, additional experiments were also carried out using hydrochloric acid. The results for 9.16 *N* and 10.24 *N* hydrochloric acid were in both cases 0.97 g. tryptophan/100 g. dry wool.

In all further work the acid used was 18.1 *N* sulfuric acid.

Effect of Temperature

The determination of the tryptophan content of the wool fabric was carried out at various temperatures; results are shown in Table III.

Interference by Other Amino Acids

The effect on the method of the other amino acids present in wool was studied by adding a large excess (30 mg.) of the acid to 30 mg. wool and 100 mg. aldehyde in 18.1 *N* sulfuric acid.

It was found that slightly high results were obtained in the presence of cystine, lysine, β-phenylalanine, and proline. On the other hand, cysteine and methionine reduced the result considerably. The 30 mg. of amino acid added to the reaction mixture represents an amino acid:tryptophan ratio of about 100:1. When this ratio is reduced to that actually present in wool, the corrections to be applied to the observed value of 0.98% are as follows.

TABLE IV. Tryptophan Content of Various Wool Samples

Wool	Fiber diameter, μ	Tryptophan content, % Root	Tip
Durban Merino	16.0	1.07	0.98
80's Tasmania	16.5	1.01	0.92
64's Geelong	17.8	0.89	—
N.Z. Merino	18.0	0.90	0.70
64's Melbourne	18.4	0.99	—
70's Victoria	18.5	1.02	0.92
64's Adelaide	19.1	0.98	0.75
East London Merino	19.7	1.03	0.91
Port Elizabeth Merino	19.8	1.01	0.72
64's Sydney	20.3	0.96	0.74
64's Queensland	20.7	1.01	0.85
64's Montevideo	21.2	0.88	0.62
64's Buenos Aires	21.3	0.97	0.72
64's New South Wales	21.6	1.02	0.61
Southdown	23.2	0.91	0.53
64's Perth	23.2	1.01	1.01
56's New Zealand	23.9	0.95	0.34
Cheviot	25.0	0.98	0.52
60's W. Australia	25.5	0.92	0.49
56/58's N.Z. South Island	26.3	0.98	0.71
44's Montevideo	27.0	0.90	0.70
56's Montevideo	30.2	0.94	0.53
56's Australia	30.9	0.90	0.46
44's Buenos Aires	31.4	0.93	0.44
44's Australia	32.1	0.93	0.75
36's	32.1	0.90	0.32
58's Buenos Aires	32.6	0.90	0.38
44/46's × Bred S. America	32.7	0.92	0.65
44's New Zealand	34.3	0.93	0.57
48's New Zealand	38.7	0.91	0.30
Lincoln	38.9	0.93	0.72

cystine	+0.005%
lysine + β-phenylalanine + proline	+0.005%
methionine	−0.003%
cysteine	−0.005%

From this it appears that the errors introduced by the various interfering amino acids cancel each other out.

For analysis using the standard conditions of 100 mg. aldehyde, 30 mg. wool, and 10 ml. 18.1 *N* sulfuric acid at room temperature, the standard error of the mean was found to be 0.003.

The Tryptophan Content of Wool Samples from Various Sources

The tryptophan content of a number of wool samples from various sources is given in Table IV. Some of these results have been reported previously [4]. The results are given for both the root and tip ends of the fibers; the fiber diameter given is that of the root end of fibers.

The results for the tryptophan contents of root wools are illustrated by Figure 1. From this it can be seen that, in general, the finer the wool the higher the tryptophan content.

TABLE V. Tryptophan Content of Fibers from Durban Merino Wool

Fiber diameter of fraction, μ	Tryptophan content, %
16.0 (average)	1.07
10–14 (fine)	1.14
20–24 (coarse)	1.03

TABLE VI. Tryptophan Content of Various Keratins

Material	Tryptophan content, %	Previous values, %
Wool (root ends)	0.88–1.14	0.7 [1] 0.94 [2] 1.45 [3] 1.8 [7] 2.1 [10] 0.5 [8] 2.3 [11]
Hair fibers from Herdwick sheep	0.48	—
Hair fibers (from Blackface sheep)	0.74	—
Wool (from Blackface sheep)	0.92	—
Cow hair	0.82	1.4 [1]
Camel hair	0.84	0.8 [1]
Cashmere	0.97	—
Human hair	0.54	0.7 [1] 1.0 [5]
Mohair	0.74	—
Cow horn	0.84	0.7 [1] 1.43 [3]
Fingernails	0.66	1.1 [1]
Pigeon feathers—Quill	1.08	—
—Barbs	0.24	—
—Pith	0.71	—
Swan feathers —Quill	0.52	—
—Barbs	nil	—
—Pith	0.66	—
Silk (degummed)	0.88	0.5 [9] 0.66 [6] 0.6 [13]
Vicara (regenerated zein protein)	nil	*0.072 [12]
Fibrolane (regenerated casein fiber)	0.4	*1.68 [12]
Gelatin	nil	0.013 [12]

* These results are for the native proteins, as no results have been published on the regenerated fibers.

The sample of Durban Merino wool was more homogeneous, as regards fiber diameter, than most of the wools examined, but there was a small percentage of fibers with a diameter appreciably lower or higher than the average. These fibers were separated by hand and the tryptophan content determined. The results are summarized in Table V.

Tryptophan Content of Other Keratins

The tryptophan contents of a number of keratins and other proteins determined by the present method

are summarized in Table VI. The values found by previous workers are given for comparsion.

Discussion

The tryptophan content of the root ends of a number of wool samples was found to be about 1%, the actual amount varying roughly with the fiber diameter or fiber quality (Tables IV and V, Figure 1). This can be shown more clearly if the fibers of similar diameter are grouped together and the average of the individual tryptophan results determined. This is shown in Table VII. The results from the larger number of samples examined in the present work thus support the initial finding of a relationship between the tryptophan content and fiber quality [4]. Of particular interest are the results in Table V, as these were obtained on a small bundle of fibers from one area of the fleece. As far as we are aware, there has been no previous report of a relationship between the fiber quality of wool and its content of an amino acid which is essential to growth.

It is unlikely that there is any appreciable destruction of tryptophan during the determination, as the same results are obtained with various strengths of both hydrochloric acid and sulfuric acid.

The tryptophan contents of the various keratin samples were found to be in the range 0.52–1.14% (Table VI). These results agree well with many of the values previously reported. The values reported by other workers in the range 1.4–2.1% were all obtained after alkaline hydrolysis and, as mentioned earlier, these results must be considered doubtful.

Acknowledgment

We wish to thank the Directors of Wolsey Limited for permission to publish this work.

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TABLE VII. Variation of Tryptophan Content with Fiber Diameter

Fiber diameter, μ	No. of samples	% Tryptophan, average
16–20	9	0.99
20–24	8	0.955
24–28	4	0.945
28–32	3	0.925
32–36	5	0.915
36–40	2	0.92

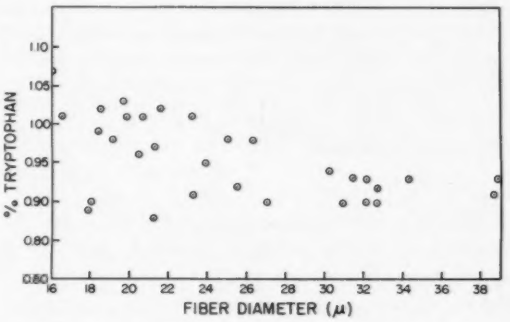

Fig. 1. Tryptophan content of wool samples.

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Manuscript received July 6, 1959.

Location of Areas of Reaction in Chemically Treated Cotton Cellulose[1]

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Abstract

The modification of cotton cellulose by environmental conditions or by chemical treatments for specific end uses ordinarily occurs at submicroscopic levels. Observations with the electron microscope have proven to be useful in delineating regions of the fiber cellulose affected by a variety of treatments, including dyeing, mercerization, acid and enzymatic hydrolysis, derivative formation, and resin impregnation. The appearance of fiber fragments treated in these ways or derived from treated fibers is illustrated and discussed.

THE LACK of homogeneity in the gross and fine structure of cotton cellulose materials often is reflected in the unevenness of distribution of modification or additive in the finished product. The failure of yarns in a fabric to dye to the same shade at crossover points as in other regions is a common example of this phenomenon. The frequently observed resistance to degradation of regions of high lateral order illustrates the small scale structural inhomogeneity of cotton. This paper is concerned with investigations of the distribution of physically or chemically modified regions in cotton to the extent that visualization by electron microscopy is able to delineate such areas. Of necessity such observations are usually limited to regions well below the fiber level in extent. This limitation does not vitiate their usefulness, since it has frequently been demonstrated that reaction or physical impregnation of regions within the fiber is necessary for optimum effects in many finishing processes. Correlation of the extent and distribution of modified areas with the end-use properties of products can lead to improvements in both product and process.

Concepts of Cotton Fiber Structure

A complete picture of the organization of the cellulose of cotton into a coherent fiber structure has not yet been achieved, although a number of valid representations have been offered. An understanding of the basic features of fiber structure is, of course, germane to a consideration of areas of reaction in the cellulose. The following illustrations review some of our present concepts of fiber structure. It will be apparent that a number of gaps remain to be filled, but a reasonably complete idea of many of the important aspects of fiber architecture has been achieved.

A single cotton fiber possesses great length–width

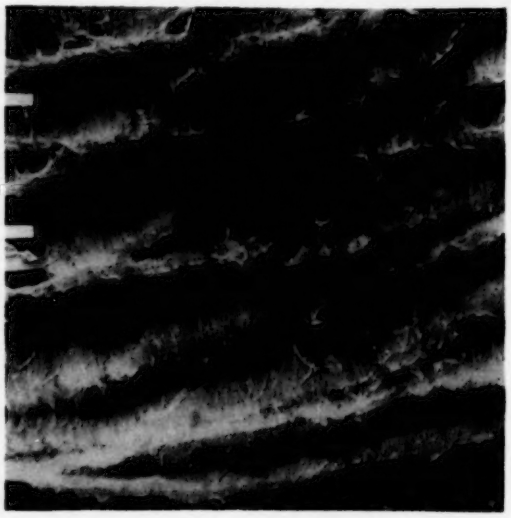

Fig. 1. Portion of cross section of cotton fiber showing separation of secondary wall into lamellae. Distance between bars is 1 μ in this figure and those following.

[1] Presented in the Electron Microscopy Session of the Princeton Meeting, Polymer and Fiber Microscopy Society, September 25–26, 1959.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

ratio, and numerous wrinkles, folds, and convolutions are present. The bulk of the cellulose of cotton (some 95%) is located in the secondary wall of the fiber, which was deposited during the period of cell wall thickening after elongation of the cell had ceased. The shape of the fiber cross section is usually some variation of that of a kidney bean. The thickness of the secondary wall cellulose, measured from the periphery of the fiber to the central canal, or lumen, varies from fiber to fiber, but is ordinarily 1–3 μ. In a single fiber, cell wall thickness is relatively constant. During the growth period, the thickness of the cell wall increases from day to day, and an examination of cross sections of fibers after treatment with swelling agents shows that the secondary wall consists of concentric rings of cellulose whose number is directly related to the age of the fiber in days. Observations of this type with the light microscope led to the concept of a lamellate arrangement of the cellulose of the secondary wall of the fiber, and this idea has been verified by examination of the cross sections of swollen fibers in the electron microscope [5].

The fiber section shown in Figure 1 was made after limited swelling, which occurs in water-soaked fibers embedded by polymerization of methyl methacrylate. Under the same conditions, a dry fiber would undergo no swelling and would present a nearly solid, continuous structure in cross section. The separation of the wet cellulose into well-defined lamellae of unswollen cellulose is undoubtedly due to differential rates of polymerization of the monomeric embedding material within and without the fiber. This phenomenon has been observed frequently in studies involving the embedding of biological tissue in acrylic resins and is considered highly undesirable. Of direct interest to us is the reflection of the structural properties of the fiber which lead to layer separation under these conditions. Since the phenomenon takes place only when the fiber is wet with water, lower alcohols, ethylene glycol, glycerol, etc., the location of polymerized methacrylate within the fiber is associated with the regions accessible to these liquids. The spaces between lamellae thus represent preferred sites for the entry of water and similar reagents. The strong lateral cohesion of the cellulose in the individual lamellae contrasts with the well-defined radial separation of these structural elements. A closer examination of the separated lamellae shows that they consist of sublamellae of parallel microfibrils, and that a single lamella is some five microfibrils thick. The total thickness of a lamella is about 0.1 μ.

The lamellate structure of the cellulose is apparently continuous throughout the length of the fiber. Few effective observations have been made of the lamellae as they are situated in an unswollen fiber, but from considerations of the optical anisotropy and x-ray diffraction patterns of cotton, it seems certain that the cellulose chains of the secondary wall are arranged in a spiral fashion, and that the direction of spiral is probably the same in all layers at any given point along the fiber length. The direction of spiral changes some 50 times along the length of the fiber, an arrangement which accounts for the numerous convolutions present in every fiber, and perhaps for the extensibility of cotton.

The microfibrils which make up a lamella of the secondary wall are nearly parallel to each other. This arrangement is illustrated in Figure 2, an electron micrograph of a typical fiber fragment obtained by the wet-beating of native cotton fibers. The finest microfibrils are about 0.02 μ wide, and perhaps one-third of this value thick. The separation of the lamella into single microfibrils is ordinarily accomplished only with extensive beating; that is, the cohesion of the fibrils is relatively strong. The apparent length of the microfibrils is indeterminate; single microfibrils 10 μ long have been observed, and this is probably not a maximum.

Fig. 2. Fragment of secondary wall of cotton obtained by wet-beating.

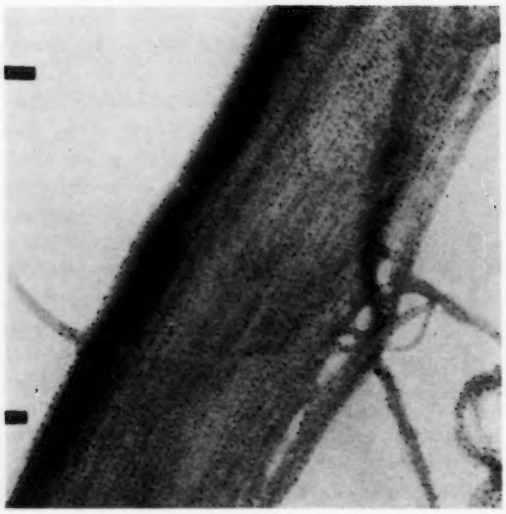

Fig. 3. Fragment of secondary wall of cotton obtained by wet-beating of fibers dyed with Congo red and exposed to lead acetate solution.

The internal structure of the native cellulose microfibril has been the subject of considerable controversy. Much of the difference in opinions on this point stems from the difficulty in making direct observations of the structure. For example, Frey-Wyssling [1] holds that the microfibril consists of an aggregate of several "micellar strands," each strand possessing a crystalline, i.e., highly ordered, core, surrounded by a paracrystalline mantle, and that this arrangement extends for considerable lengths along the microfibril. Hess [3], on the basis of low-angle x-ray scattering and electron microscopical examination of certain iodine-stained celluloses, proposes regular alternation of regions of high and low lateral order along the length of the microfibril. A discussion of various types of observations has been published by Hock [4], in which the limits of error and the dangers of extrapolation of limited data on the question are pointed out. Hock's interpretation leads to a picture of microfibrils consisting of regions of relatively high lateral order interrupted by distortions and irregularities having low order. This point of view has been independently extended and modified by Hearle in an ingenious manner [2].

Observations on Modified Fibers

Dyeing

The application of many dyes to cotton is accompanied by a minimum of chemical change in the cellulose of the fiber. Substantive dyes, for example, are believed to be held to the cellulose by hydrogen bonding effects only. Visualization of the location of such materials in the fiber by electron microscopy cannot be accomplished because of the lack of difference in the electron-scattering properties of the dye and the cellulose. The sulfonic acid groups present in many substantive dyes permit attachment of heavy atoms, however, and in this way the presence of the dye may be made apparent. Figure 3 shows a fragment derived from cotton which had been dyed with Congo Red and subsequently treated with a 10% solution of lead acetate. The preparation of the specimen involved vigorous washing prior to examination in the electron microscope. The dark spots are regions of high concentration of Pb, which had been insolubilized as the salt of the dye. The dark areas are about 100 Å in diameter, and are obviously confined to the cellulose. They show a strong orientation in the direction of the microfibrillate pattern of the fragment. If we can assume that there has been no migration of the Pb during preparation of the specimen, then observations of this type can be used to locate concentrations of substantive dyes at the microfibrillate level in cellulose.

Many vat dyes are known to be agglomerated in the dyed fiber into particles containing a large number of dye molecules. An examination of several vat dyed cottons did not disclose the location of such particles, but a specimen dyed with Novanthrene [3] Brilliant Scarlet RK yielded the micrograph in Figure 4. The regular distribution of dark particles along lines corresponding to the pattern of microfibrillate texture in this ultrathin section of dyed cotton shows a homogeneous distribution of the vat dye similar to that observed for the substantive dye in Figure 3. The size of the dark areas is approximately 500 Å. Larger irregularly shaped particles present may or may not be the vat dye also.

Mercerization

The widely practiced treatment of cotton with strong NaOH solutions is an example of physical modification of the cellulose with little or no chemical change. The extent of conversion of the cellulose I crystal lattice to cellulose II is known to be profoundly influenced by the tension existing in the

[3] The use of trade names does not imply endorsement by the Department of the products of one manufacturer over those of other manufacturers.

fiber during treatment. The effects of 20% NaOH solution on cotton treated in different physical states is shown in the micrographs of Figure 5. At the left, a fragment of cotton similar to that shown in Figure 2 was exposed to the NaOH solution. Little or no tension on the cellulose structure existed under these conditions, and the fragment shows a somewhat swollen appearance, with strong crimping of the individual microfibrils. In the micrograph at the right, a fragment obtained from a fiber exposed without restraint to 20% NaOH prior to wet-beating is seen. A comparison with Figure 2 shows that the microfibrillate texture exhibits a swollen appearance, but there is much less crimping of the microfibrils than when the fragment itself was exposed. When fragments obtained from mercerized fabrics are examined, it is difficult to discern the characteristic features noted in the micrographs in Figure 5. The tension existing in each of these specimens during exposure to NaOH varies in a predictable manner, and the extent of swelling and crimping of the microfibrils appears to be strongly dependent on this factor. The inhibition of diffusion must also be considered in this connection.

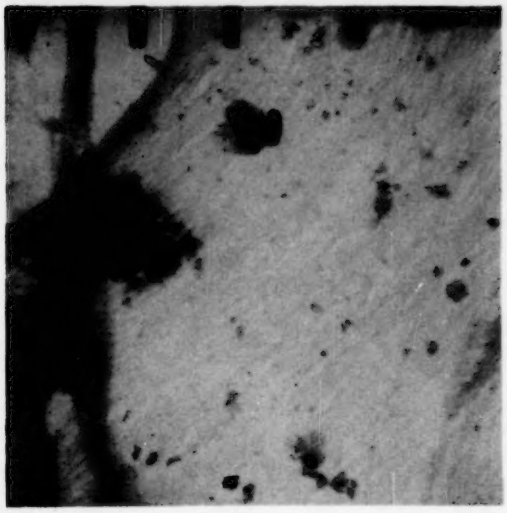

Fig. 4. Fragment of secondary wall of cotton from specimen dyed with a vat dye, Novanthrene Scarlet RK.

Hydrolysis

The existence of regions in cotton cellulose more readily susceptible to chain scission by mineral acid solutions has been demonstrated frequently. The transverse breakdown of the microfibrils into particles of the order of 1000 Å in length has led to the identification of these particles with the regions of high lateral order of the chain molecules. Exposure of cotton to cellulolytic enzyme systems leads to results similar to those obtained with acids, except for their occurrence in a much more localized manner. The diffusion of hydrogen ions through cellulose structures is much more rapid than would be the case with the relatively enormous protein complex of the cellulase. Nevertheless, there is a striking similarity in the submicroscopic appearance of

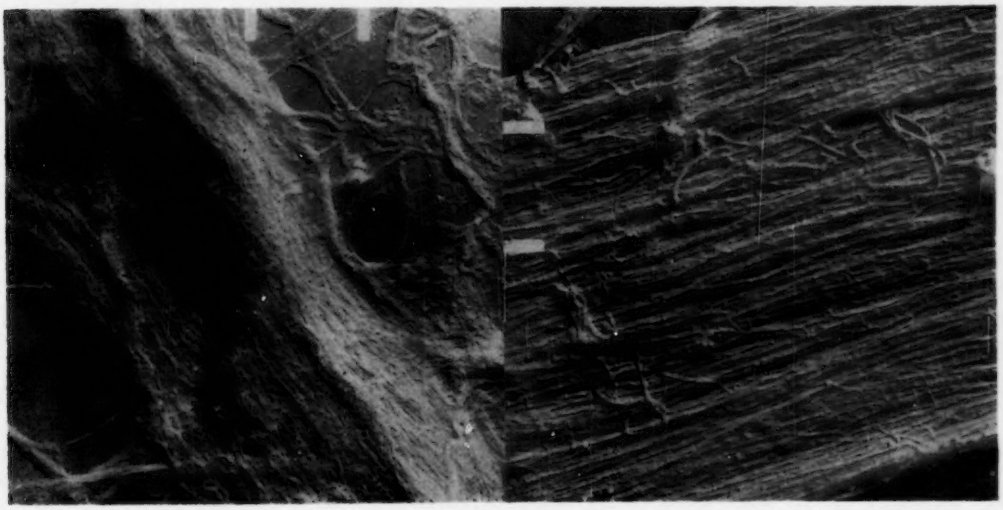

Fig. 5. Fragments of cotton treated with 20% NaOH in the fragmented state (left) and in the intact fiber state (right).

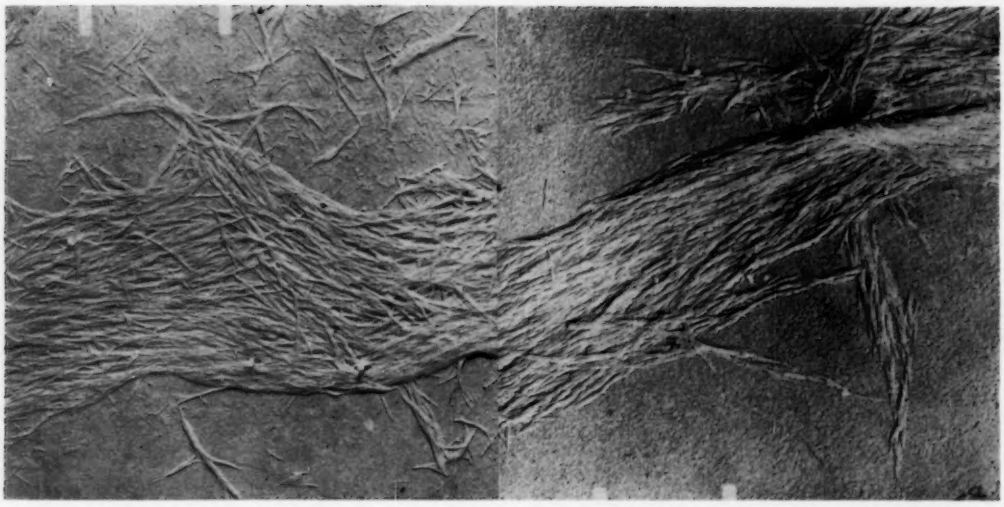

Fig. 6. Fragments of cotton exposed to 10 *M* sulfuric acid (left) and to extract of cellulolytic fungus *Myrothecium verrucaria* (right).

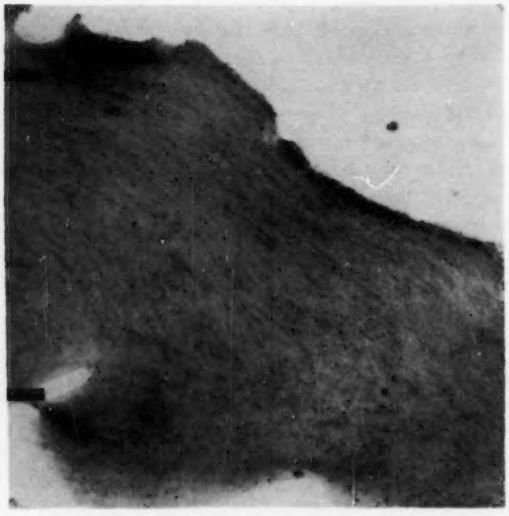

Fig. 7. Thin section of carboxymethylated cotton fiber (DS 0.1) treated with lead acetate solution.

cotton exposed to each of these reagents, as illustrated in Figure 6. On the left is a fragment obtained from fibers exposed to 10 *M* H_2SO_4 at 25° C. for 136 hr.; on the right, a fragment exposed for 16 hr. at room temperature to the cellulase-containing extract of the fungus *Myrothecium verrucaria*. In both cases there is a well-defined etching of the original continuous fibrillate texture of the cellulose. In the fragments shown here, there is not much breakdown of the spatial relationships of the microfibrils usually observed in fragments obtained by wet-beating of cotton.

Formation of Derivatives

The submicroscopic features of cotton cellulose show no discernible change in the electron microscope when the degree of substitution (DS) of the chemically modified product is low, unless covalent cross-linking of the cellulose chains occurs. The introduction of hydrophobic groups (e.g., acetyl) reduces the tendency of fibers to fibrillate on wet-beating, but this is noticeable only when the DS is 1 or more [6]. Hydrophilic derivatives beat apart rather more easily than untreated cotton, but their appearance is similar to it in most respects. When the derivative contains reactive functional groups (e.g., carboxyl), a heavy atom can be introduced to produce contrast in the electron microscope image. Figure 7 shows an ultrathin section of a carboxymethylated cotton fiber (DS 0.1) treated with lead acetate. The dark areas, representing concentrations of the insoluble Pb salt, are seen to be distributed along lines corresponding to the microfibrillate pattern previously established in the observations mentioned above. It is interesting that some areas of the cellulose have not taken up the lead to a noticeable degree, although the formation of this derivative involves strong swelling and presumably intermicellar reaction.

The increasingly widespread use of N-methylol

compounds to impart wrinkle recovery and dimensional stability to cotton involves the formation of derivatives containing reducing groups. The location of the areas where these groups are present can be revealed by the formation of reduced metals such as silver and osmium. The precipitation of reduced silver, using Tollens' reagent, is followed by growth of the silver crystals formed. Presumably migration from the original site of precipitation occurs with time, as the fibers on which this test is carried out develop strong dichroism. When colorless osmium tetroxide is reduced by heating such fibers in a 0.1% solution at 90° C. for 15 min., the fibers darken to a brown or black color. Figure 8 shows a portion of an ultrathin section of a fiber containing 3.5% dimethylol ethyleneurea after treatment with osmium tetroxide. The distribution of osmium appears to follow the lamellate pattern of the fiber cross section, but the radial distribution indicates that the methylol derivative formation occurs *within* the individual lamellae as well as between them.

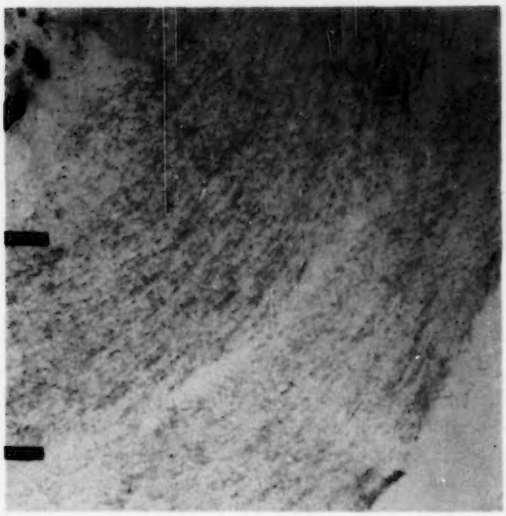

Fig. 8. Thin section of cotton fiber treated with dimethylol ethyleneurea (3.5% add-on) and with osmium tetroxide.

Impregnation vs. Reaction

Numerous finishing operations applied to cotton involve simple impregnation of or reaction with the cellulose. A combination of these conditions may also be the case, particularly with polymer-forming reagents. Impregnation and polymerization without reaction with the cellulose is illustrated in Figure 9. At the left, an ultrathin section of a fiber in which poly(methyl methacrylate) had been deposited is shown after removal of the polymer. It is similar to Figure 1 in all respects. At the right is a cross section obtained from the same specimen, in which the cellulose has been removed by solution in cupriethylenediamine hydroxide, leaving behind the acrylic polymer phase of what was a simple cellulose-resin mixture. The resin residue thus represents an *in-*

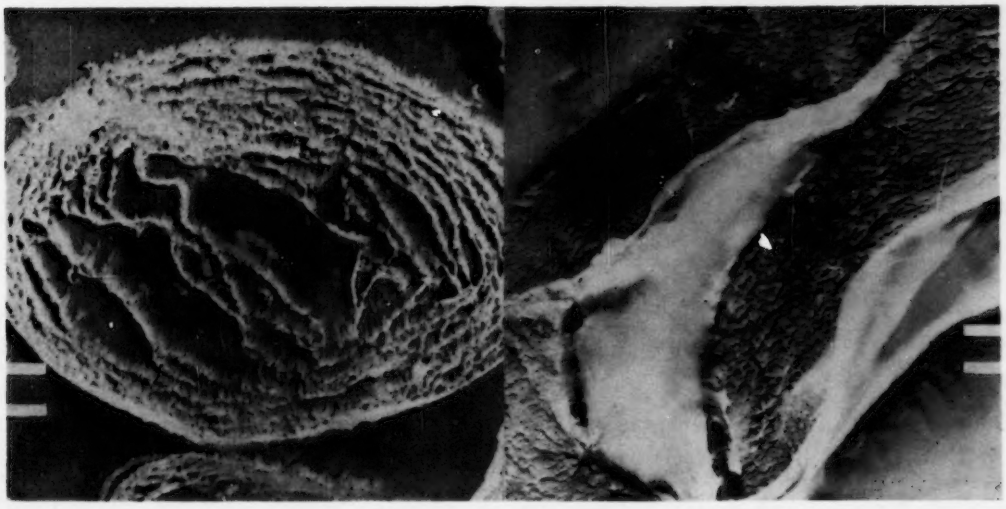

Fig. 9. Residues of cross sections of cotton fibers impregnated with poly(methyl methacrylate) after removal by solvent of acrylic resin (left) and cellulose (right).

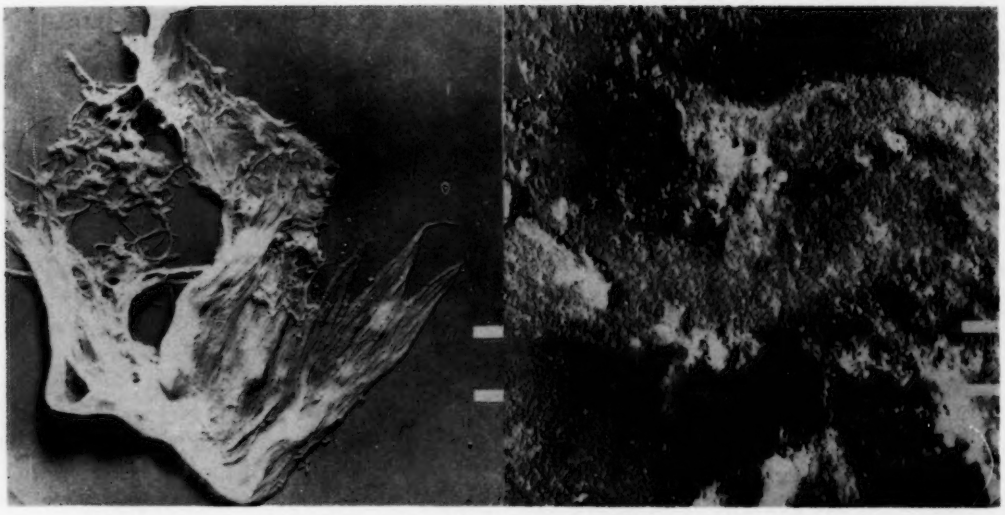

Fig. 10. Fragments of cotton containing 10% methylol melamine resin before (left) and after (right) exposure to cupriethylenediamine hydroxide.

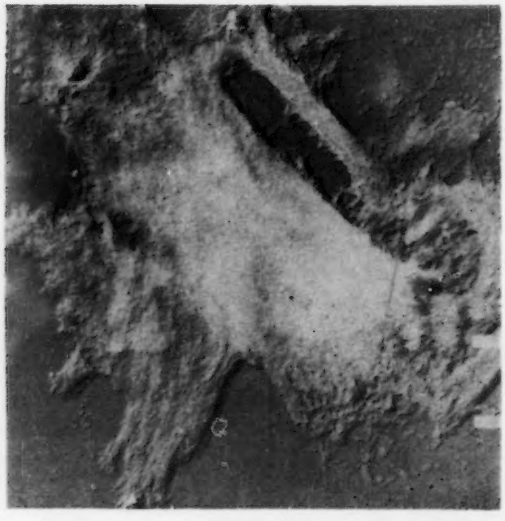

Fig. 11. Fragment of cotton containing 10% dimethylolurea after exposure to cupriethylenediamine hydroxide.

ternal replica of the lamellate fibrillate structure of the fiber.

Exposure of modified cottons to cellulose solvents has been useful in delineating areas of derivative formation of impregnants in the fiber structure. Figure 10 (left) shows a typical fragment obtained by wet-beating fibers containing 10% methylolmelamine resin in which reaction with the cellulose had been minimized by the conditions of treatment. At right is the residue of a similar fragment after exposure to cupriethylenediamine hydroxide. There has been relatively little swelling of the cellulose; the residue is granular, and there has been considerable loss of material by solvent action. In contrast, fragments of cotton containing 10% dimethylolurea, a reagent forming covalent cross links between cellulose chains, displays relatively good stability toward the cellulose solvent. The residue of such a fragment is shown in Figure 11.

Discussion

The examination of modified cotton cellulose in the electron microscope suggests that the main features of the model structural arrangements proposed by Frey-Wyssling [1] for cellulose and by Hearle [2] for linear polymers are valid. Substantive dyes insolubilized by conversion to lead salts appear to be concentrated on and possibly in the individual microfibrils. The frequency of areas of concentration is relatively high in the specimens observed, but the strong possibility exists that the areas in adjacent microfibrils are "out of phase," so that the distance between dye concentrations may be considerably greater than that observed. The etching of the cellulose structure by acids and cellulases continues until well-defined individual particles of variable length are visible. Hence, the regular spacing of accessible regions along the microfibrils suggested by Hess [3] does not appear to hold for cotton cellulose. Hearle's

picture of random discontinuities in the well-ordered regions along the microfibrils seems more appropriate. The sharpening of the outlines of cellulose structures attacked by acid is consonant with the existence of a poorly-ordered surface region on the microfibrils. The relative constancy of width of individual residual fibrillate structures observed after acid hydrolysis does not support Hearle's concept of branching regions of high lateral order, but almost all pictures show definite evidence of anastomosing fibrillate texture.

Mercerization of cotton, with its attendant swelling, distortion, and shrinkage, appears to extend well into the interior of the microfibrils when the cellulose structure is free from restraint. The crimping of the original straight arrangement of the microfibril bundles leads to a structure which will have high extensibility, a property frequently noted in cotton mercerized without tension. The visible texture of the cellulose after mercerization is more fluffy, implying a decrease in density of packing of the structural elements. This change is reflected in the increased uptake of dyes and higher reaction rates in many chemical processes.

The introduction and subsequent polymerization of acrylic esters extends to the microfibrillate level in cotton cellulose. The accurate "replication" of the microfibrillate texture within the lamellate structure of the fiber indicates that molecules of the dimensions of methyl methacrylate can reach this level in the fiber, if carried in by a polar liquid. Restriction of reactant molecules such as the N-methylol compounds used for wrinkle resistance to the regions between lamellae of the fiber does not seem to occur. Removal of cellulose from fragments and cross sections [7] of chemically modified cotton indicates that a substantial amount of the cellulose has been rendered insoluble by conversion to the cross-linked state. If this conversion were to occur only in the surface regions of the lamellate structure, a much larger amount of cellulose would be removed by treatment with cellulose solvents.

In summary, areas of reaction in modified cotton cellulose can be observed by changes in shape, contrast, or solubility of suitable specimens examined in the electron microscope. The methods of examination outlined here are elementary in character and involve the use of assumptions which may not be completely valid. Nevertheless, such observations serve a useful and important purpose in extending our knowledge of the relationship of the microscopic and submicroscopic domains of cotton textiles and their response to various environments.

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Manuscript received September 25, 1959.

Letters to the Editor

A Nomogram for Use with the Vibroscope

Department of Physics and Mathematics
Division of Engineering
Lowell Technological Institute
Lowell, Massachusetts
October 9, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In the use of the Vibroscope, the weight per unit length of a completely flexible fiber can be calculated directly if the natural frequency of transverse vibration is measured when a known length of fiber is held under a given tension. For such a fiber, the linear density m of the fiber is given directly in CGS units by

$$m = \frac{T}{4f^2l^2} \qquad (1)$$

wherein T is the tension force, f is the fundamental resonant frequency, and l is the free length of the fiber.

In usual laboratory practice, the linear density is reported in denier units, and the tension weight is in terms of grams rather than dynes. To convert Equation 1 to deniers, it is necessary to multiply m by 980, then by 0.9, and finally by 10^6. If these arithmetic operations are performed, Equation 1 may be rewritten as

$$de = \frac{220500000\,g}{f^2l^2} \qquad (2)$$

wherein de is the denier of the fiber, g is the tension weight in grams, and l and f are as given previously.

The forms of Vibroscopes in common use operate on the principle of variable tension at a fixed frequency or of variable frequency with a fixed tension. Regardless of which type of Vibroscope is employed, a certain amount of arithmetic is involved in order to obtain the desired answer. The solution of Equation 2 for a large number of fiber specimens using a desk calculator thus can become a tedious operation. With this in mind, a set square nomogram [1] was constructed satisfying most conditions of use; it is reproduced herewith. A clear piece of thin sheet plastic or vellum or tracing cloth, at least 15 in. square, is needed to use the nomogram. Two lines, dividing the sheet into quarters diagonally, should be carefully scribed on the sheet at exactly right angles to each other. This sheet is called the set square sheet.

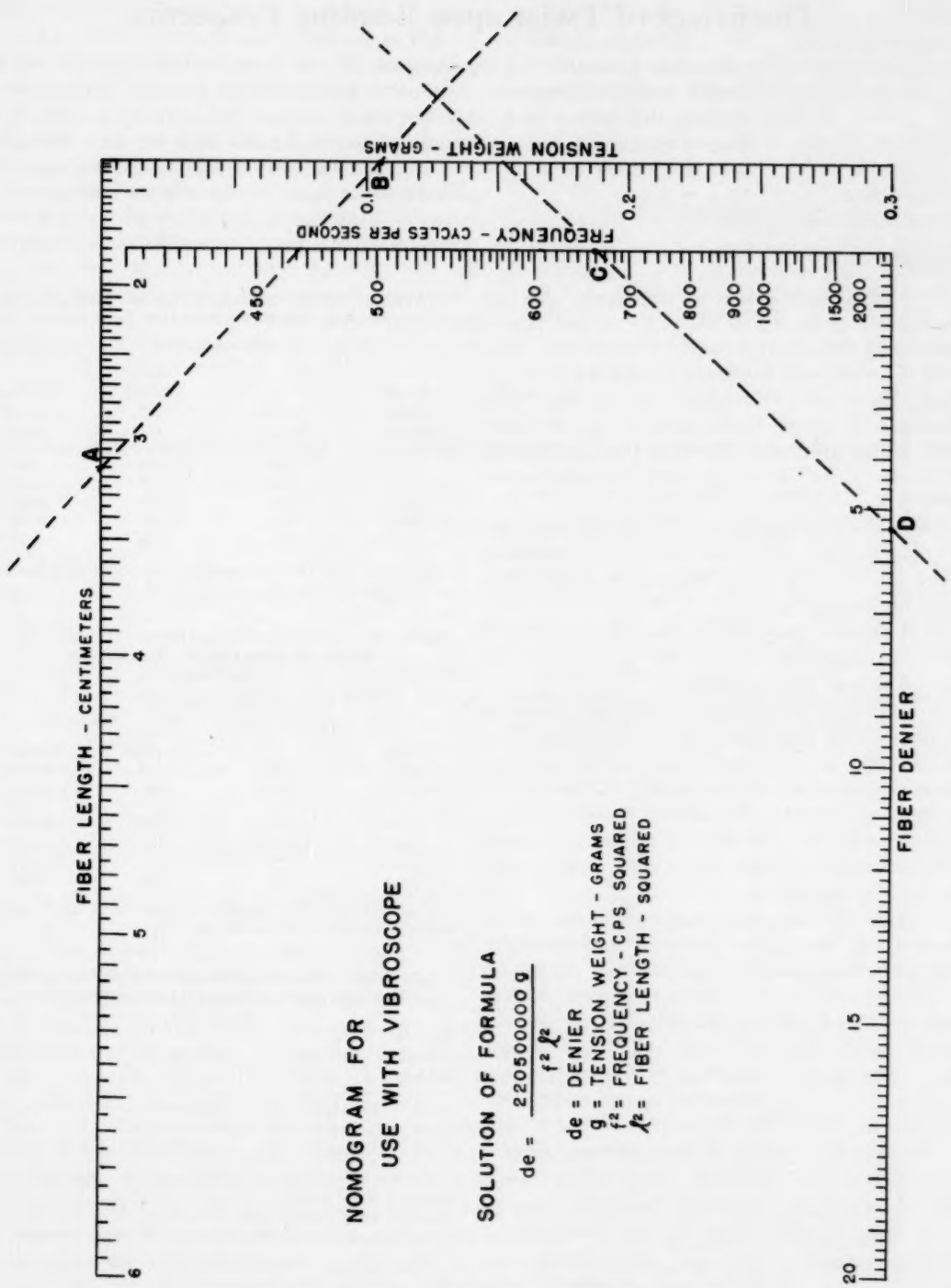
To use the nomogram, the set square sheet is superimposed on the chart and one of the lines, AB, is oriented so that it connects the measured fiber length and the tension weight. The set square sheet is then slid parallel to the line AB until the other line CD simultaneously passes through the measured frequency value. The extension of this second line intersects the denier scale, and the denier is read off at the intersection. Thus, for the illustration given on the nomogram, the measured fiber length was 3.15 cm., the tension weight was 0.105 g., and the resonant frequency was 660 cycles/sec. The resulting denier read from the nomogram is 5.4, whereas the calculated denier is 5.36, a difference of less than 1%.

Care should be taken not to misread the chart. If the line AB were used to read the fiber length and frequency scales, and the line CD to read the tension weight and denier scales, the wrong answer would be obtained. This mistake can be avoided if it is borne in mind that each straight line on the set square sheet is used to read two scales which meet in a point. The scales for fiber length and frequency do not meet in a point and must not be read with the same straight line.

Large scale copies of the nomogram are available from J. K. Frederick, Jr., Professor and Chairman, Division of Textiles, Lowell Technological Institute, who brought the need for such a nomogram to the attention of the writer, and to whom the writer is indebted for technical advice.

L. IVAN EPSTEIN

[1] See L. I. Epstein: Nomography (Interscience Publishers, New York, 1958), Section 5.5.


FIBER LENGTH - CENTIMETERS
TENSION WEIGHT - GRAMS
FREQUENCY - CYCLES PER SECOND
FIBER DENIER
A
B
C
D
NOMOGRAM FOR
USE WITH VIBROSCOPE
SOLUTION OF FORMULA
de = 220500000 g / f² ℓ²
de = DENIER
g = TENSION WEIGHT - GRAMS
f² = FREQUENCY - CPS SQUARED
ℓ² = FIBER LENGTH - SQUARED

The Effect of Twist upon Bending Properties

Courtaulds, Limited
Textile Research Laboratory
Bocking, Braintree
Essex, England
October 13, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A detailed investigation of the factors affecting the bending properties of fibers, yarns, and fabrics has recently been carried out in this laboratory. We were therefore very interested to read the paper by Platt, Klein, and Hamburger [3] entitled "The Mechanics of Elastic Performance of Textile Materials. Part XIV: Some Aspects of Bending Rigidity of Singles Yarns" and to compare their conclusions with ours.

Our theoretical approach, while in some ways not as rigorous, led us to the following conclusions, which are similar to those obtained by Platt, Klein, and Hamburger.

1. If filament movement is possible in a yarn of very low twist, yarn flexural rigidity should be the sum of filament flexural rigidities.

2. Inhibition of filament movement, however, should increase yarn rigidity up to a theoretical limit of the order of N_f/p times that that for complete freedom (where N_f is the number of filaments in the cross section and p the packing factor).

3. Provided that the ease of filament movement remains unaffected, yarn twist should cause a slight decrease in yarn rigidity.

A range of spun and continuous filament viscose rayon yarns was then examined experimentally. The yarns were tested as received from the spinner or thrower, except that in order to prevent snarling, they were set at 80° C. and 80% RH for an hour before conditioning and testing at 22° C. and 65% RH. The loop test described by Carlene [1] was used, and the results expressed as equivalent bending lengths (defined by Peirce [2]), taking account of the increase in denier of the continuous filament yarns due to yarn retraction. Some of the results are shown in Tables I and II. The values obtained were close to those expected for independently-bending filaments, which were deduced from Carlene's data [1]. As will be seen, the effect of twist was found to be small and no approach to the theoretical upper limit (in this case of the order of 10 cm.) was detected, although slight increases in stiffness were sometimes observed with the higher twists. It must therefore be assumed that under the conditions of measurement, considerable redistribution of strains along the length of the filament is possible. The extent of redistribution is presumably

TABLE I. 300/50 Continuous Filament Viscose Rayon Bending Lengths Deduced from Loop Tests

10 Tests/sample

Actual twist, turns/in.	Actual denier	Mean bending length, cm.	Standard error of mean
2.3	304	2.89	0.04
8.5	300	2.95	0.03
19	315	2.95	0.07
26	336	3.21	0.08
39	362	3.08	0.10

Expected value for independent filaments: 2.90 cm.; expected upper limit of the order of 10 cm.

TABLE II. 1/20s Spun Viscose Rayon (1½ den., 1.7/16 in. Staple) Bending Lengths Deduced from Loop Tests

20 Tests/sample

Actual twist, turns/in.	Twist factor	Mean bending length, cm.	Standard error of mean
13.8	3.1	2.08	0.05
15.7	3.5	1.97	0.05
17.6	4.0	2.07	0.03
20.3	4.5	2.44	0.09

Expected value for independent fibers: 2.04 cm.; expected upper limit of the order of 10 cm.

TABLE III. Continuous Filament Viscose Rayon Fabrics Bending Lengths Deduced from Cantilever Tests

cm. ± 0.03

Approx. twist, turns/in.	150/27 yarn			150/40 yarn			150/72 yarn		
	1	2	3	1	2	3	1	2	3
3	2.50	2.18	2.34	2.36	1.96	2.16	2.58	1.67	2.13
6	2.42	2.16	2.29	2.31	1.96	2.11	2.25	1.63	1.94
12	2.39	2.19	2.29	2.15	1.91	2.03	2.08	1.65	1.87

Column 1—warp strip; 2—weft strip; 3—mean of 1 and 2. Nominal setts* in loom (per inch)—66 × 66. Preparation of fabrics: desize, scour, wash-off and dry. Crease-resist treatment used urea-formaldehyde dope with added softener.

* The same as "texture" of a fabric; the number of warp ends and filling picks in woven fabrics.

affected by the lubrication of the filament surfaces, but such removal of spinning lubricant as was effected by a scouring treatment or prolonged soaking in petroleum ether was found to have little effect.

When a yarn forms part of a fabric, the frictional forces between the filaments may be affected by the tightness of the structure and the finish of the fabric. Very complex effects are therefore possible. The results given in Table III, however, bear out the expected effects of filament denier and yarn twist in a series of viscose rayon filament fabrics which had been given a uniform crease-resistant treatment. With such a finish, easy filament movement would be expected. Work on further systematic series of fabrics has shown that, when filament movement is inhibited by fabric tightness or adhesion between the filaments, the effect of filament denier is masked but an additional effect of fabric tightness is noted. Yarn twist can still have a slight effect.

It is hoped to publish a full account of this work in due course.

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D. N. E. COOPER

The Felting of Wool in Concentrated Solutions of Electrolytes

Abbey Meadow Mills
Leicester, England
July 6, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

We have investigated the felting of wool in calcium chloride and zinc sulfate solutions of various concentrations; our results support the view of Bogaty, Sookne, and Harris [1] that felting is reduced when the water content of the solution is reduced.

The wool fabric used was knitted from a 64's yarn and was scoured before use with Lissapol N (ICI).

The shrinkage tests were carried out in a "Whirldry" washing machine manufactured by the Easy Washing Machine Corporation, Syracuse, N. Y. The machine has been described in another publication [2]. We have found that the results obtained with this machine are highly reproducible, as mentioned in this publication; statistical analysis shows that a difference of 0.4–0.6% between mean results of about 20% area shrinkage is likely to be significant. Two samples of untreated wool were washed in each experiment; the mean results are recorded in the table and figures that follow.

The calcium chloride and zinc sulfate used were of a good commercial grade and were the anhydrous salt and heptahydrate respectively.

In a solution of a hydrated salt, such as calcium chloride, the water can be present in two ways: as water of hydration (i.e., the water required to form $CaCl_2 \cdot 6H_2O$) and as the "free" water or the water remaining after formation of the hydrate. If the shrinkage results for washing 30 min. at 25° C. are plotted against the amount of "free" water present in the solutions, an interesting result is obtained, as shown by Figure 1.

A somewhat similar result was obtained on washing a different sample of wool in aqueous alcohol of various concentrations. The lower shrinkage results

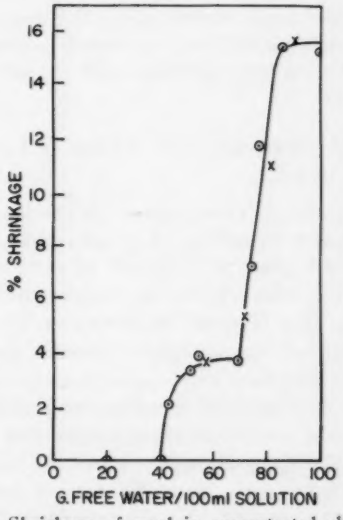

Fig. 1. Shrinkage of wool in concentrated electrolyte solutions; ⊙-⊙-⊙, $CaCl_2$; ×-×-×, $ZnSO_4$.

TABLE I. Shrinkage of Wool in $CaCl_2$ Solutions at Various Temperatures

Temperature, °C.	Shrinkage, %, after washing for 30 min.	
	In the presence of $CaCl_2$	In the absence of $CaCl_2$
17	−0.2	18
31	−0.2	27
42	1.8	37
50	5.6	35
56	8.1	34
73	9.8	32
86	9.9	32
93	29.5	32

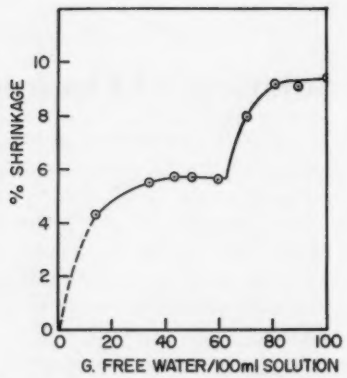

Fig. 2. Shrinkage of wool in aqueous ethanol solutions.

obtained in this set of experiments are probably due to the lower temperature and the fact that the experiments were carried out in neutral solutions. The results for 60 min. washing at 20° C. are shown in Figure 2.

Effect of Temperature on Milling in Concentrated $CaCl_2$ Solutions

The results in Table I show the shrinkage of wool in a solution containing 48 g. anhydrous $CaCl_2$ and 1 g. glacial acetic acid/100 ml. at various temperatures. The results given for washing in the absence of $CaCl_2$ were obtained in another series of experiments carried out at slightly different temperatures and are therefore only approximately comparable with the data obtained in the presence of $CaCl_2$.

It can be seen from these results that shrinkage begins at some temperature above 31° C., becomes more definite above about 50° C., but does not become normal until 93° C. The results in the preceding section show that the shrinkage of wool appears to depend on the free water content of the solution. The fact that wool begins to shrink in strong calcium chloride solutions above about 30° C. could be due to an increase in the "free water" content of the solution; it is of interest that the hexa and tetra hydrates have transition temperature of about 30° C. and 50° C. respectively [4].

There is, however, no obvious explanation, in terms of hydrate transitions, for the fact that felting becomes normal at temperatures above about 90° C.

Discussion

The above results suggest that there must be a minimum amount of water present for wool to shrink and that it is necessary to have 70–80% free water in the solution for the shrinkage to be normal. If the results are interpreted as suggested above, they can be taken to provide evidence on the important role played by water in the shrinking of wool.

Bogaty, Sookne, and Harris [1, 5] have shown that the felting of wool in various electrolyte solutions is more closely related to the elastic properties of single fibers than to their frictional properties. The results of the few single fiber experiments that we have carried out are in agreement with their results. This emphasizes the important part played by the elastic properties in the shrinkage of wool.

Preston [3] has shown that if the viscosity of the felting solution is increased there is a reduction in the felting shrinkage. He found that to eliminate felting completely it was necessary to increase the viscosity to 300 cp., whereas in our experiments felting was eliminated by solutions of much lower viscosity (20 cp). From this it would appear that the reduction in felting reported in this work is not directly connected with the increase in viscosity of the solution.

We wish to thank the Directors of Wolsey Limited for permission to publish this work.

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D. R. GRAHAM
K. W. STATHAM

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